**Graphdiyne-Stabilized Silver Nanoparticles as an Efficient Electrocatalyst for CO₂ Reduction**

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Electrochemical CO₂ reduction reaction (e-CO₂RR) into high-value chemicals is a promising approach for sustainable energy research, but there remains a great challenge to develop efficient and stable catalysts. Herein, in situ synthesized uniform Ag nanoparticles (AgNPs) directly growing on the surface of 2D graphdiyne (GDY) for selectively reducing CO₂ to CO with high efficiency and stability are reported. Due to the special electronic distribution of GDY, it not only serves as a template for the growth of AgNPs to prevent its aggregation, but also increases active sites and transformation of electrons through the intimate interaction between phase interface to enhance their cooperative catalytic effect, which highly improves the electrocatalytic performance of the nanocomposite. Through investigations, it is found that the Ag/GDY/CC nanocomposite electrochemically reduces CO₂ to CO with Faraday efficiency up to 92.1% and current density of 25.74 mA/cm² at the potential of −1.3 V versus reversible hydrogen electrode (RHE). Meanwhile, during catalysis, the Ag/GDY/CC composite maintains excellent stability with a high current density of ≈26 mA/cm² (threefold higher than that of Ag/CC), unchanged for over 24 h. To the best knowledge, herein, the first experimental study of an efficient CO₂ reduction electrocatalyst based on GDY is represented.

1. Introduction

As of May 2020, the carbon dioxide content in air was 418.12 ppm, which had grown by 2.48 ppm compared with May the previous year.[1,2] With the overuse and depletion of fossil fuels, the resultant rising carbon dioxide content is seriously damaging the environment and making the climate worse. Thus, it is highly desirable to develop an advanced strategy of converting carbon dioxide into high-value and sustainable energy resources.[3] Among numerous development strategies, electrocatalytic carbon dioxide reduction reaction (e-CO₂RR) is considered to be an extremely promising approach, as it can utilize the surplus power generated by renewable energy to complete the conversion of CO₂ under mild conditions.[4,5] Nevertheless, electrocatalytic CO₂RR still suffers from multiple shortcomings, such as diversified reduction products, high reduction overpotential, low-energy utilization, poor catalyst stability, and so on, which severely inhibit the industrial application of catalysts.[6–8] Simultaneously, hydrogen evolution reaction (HER) remains a strong competitive reaction in CO₂RR, especially in aqueous systems, as the theoretical reduction potential of HER is lower than that of CO₂RR.[9] Therefore, it is essential to develop and design high-functional electrocatalysts to solve the problems earlier.[10,11]

So far, transition metal Ag has been considered to be one of the most promising candidates for catalytic CO₂RR, particularly for electrocatalytic reduction of CO₂ to CO, which is a valuable industrial feedstock for many chemicals and fuels.[12–16] With various unique morphologies and configurations, Ag-based electrocatalysts for CO₂RR have been widely studied due to their high catalytic activity, selectivity, and low costs for CO₂-to-CO reduction compared with other precious metal materials such as Au.[17] The Ag-based thin films with different stacking modes and crystal plane orientations were studied and exhibited great catalytic...
activities for electrochemical CO$_2$-to-CO conversion due to their film surface structures that could support the formation and stabilization of the COOH$^\cdot$ intermediate.\cite{18-20} A series of Ag-based nanowires (Ag-NWs) has been prepared as electrocatalysts for CO$_2$-to-CO reduction, which achieved high Faradaic efficiencies (FEs), mostly due to the increased electrochemically active surface area.\cite{21-23} Mauzeroll and coworkers biosynthesized Ag-based nanorings (Ag-NRs), which could reach an FE of 95.0\% for the conversion of CO$_2$ to CO.\cite{24} Polyansky’s group reported a Ag nanocoral catalyst with a high surface area, displaying a low overpotential of 0.37 V and high current efficiency of 95\% for CO$_2$-to-CO reduction catalysis.\cite{25} In addition, some other nanoporous Ag-based (np-Ag) catalysts with diverse nanostructures have also been investigated for electrocatalytically reducing CO$_2$ to CO with significantly enhanced catalytic efficiency.\cite{26-29}

Nevertheless, in all sorts of morphologies, Ag-based nanoparticles (AgNPs) have received extensive attention for the research of driving electrochemical CO$_2$RR to CO. Due to the particle size effect, morphological effect, and intrinsic activities of AgNPs, they could exhibit remarkable electrocatalytic performance in CO$_2$RR to CO.\cite{30,31} At this stage, it is still highly desired to develop a practical strategy to optimize the activity, selectivity, and stability of the Ag composite materials.\cite{32-35}

As a new type of functional carbon material, since it was first synthesized by Li et al.,\cite{36-39} Graphdiyne (GDY) has been successfully applied in numerous research areas, such as HER\cite{40-42}, oxygen evolution reaction (OER),\cite{43-45} nitrogen reduction,\cite{46} supercapacitors,\cite{47} lithium- and sodium-ion batteries,\cite{48-51} CO$_2$ reduction,\cite{52-54} and so on.\cite{55} With the unique high $\pi$-conjugated construction, GDY possesses very high electronic conductivity ($2.56 \times 10^{-1}$ S m$^{-1}$), excellent charge carrier mobility ($2 \times 10^{5}$ cm$^2$ V$^{-1}$ s$^{-1}$), and furthermore, superior stability under acid or alkaline conditions at up to 150 °C.\cite{39} Therefore, in the field of electrocatalysis, GDY-based materials not only exhibit high catalytic activities but also maintain excellent stability. Due to the special layered 2D space configuration, high-electron cloud density, uniformly distributed pores, and highly conjugated electron distribution of GDY,\cite{56-63} However, up to now, only a few theoretical studies of GDY-based materials have been reported for the electrocatalytic reduction of carbon dioxide.\cite{54,62-63}

AgNPs supported with various substrates as electrocatalysts have displayed outstanding performances.\cite{13} In the meantime, it is still required to develop robust electrocatalysts for CO$_2$ conversion with enhanced activity and selectivity. In consideration of the outstanding features of GDY in electrocatalysis and the promising potential application of silver nanoparticles in electrochemical CO$_2$RR, in this study, a unique GDY-stabilized silver nanoparticles (AgNPs/GDY) composite is constructed in situ and thoroughly investigated as a catalyst toward electrochemical CO$_2$RR to CO with excellent activity, selectivity, and stability. By the direction and restriction of the GDY substrate, around 30 nm regular-sized AgNPs uniformly disperse on it directly, which prevents the aggregation of the AgNPs. Meanwhile, the special configuration and electron distribution of GDY can fundamentally regulate and activate the AgNPs, which enable the AgNPs and GDY to synergistically electrocatalyze CO$_2$RR to CO with high Faraday efficiency of 92.1 \% and long-term stability of up to 24 h. More importantly, the composite can maintain the large current density at around 26 mA/cm$^2$ unchanged during electrolysis due to the synergistic effect of AgNPs and GDY. The (111) plane of AgNPs is regarded as the most promising plane for reducing CO$_2$.\cite{21,26,28} The in situ anchoring of AgNPs onto the GDY template with intimate contact can highly increase the exposure of the Ag (111) plane of the AgNPs and fully increase the surface charge density of AgNPs, thus tremendously enhancing its performance for the electrocatalytic reduction of CO$_2$ to CO.

2. Results and Discussion

2.1. Synthesis and Characterization of Ag/GDY/CC

As shown in Scheme 1, the Ag/GDY catalyst was synthesized in three steps. First, tetrabutylammonium fluoride was added to hexakis(trimethylsilyl)ethynylbenzene to remove the trimethylsilyl groups to obtain the hexaethynylbenzene (HEB) precursor under Ar atmosphere. Second, in the dark, GDY grew on the surface of copper foil through cross-coupling reaction at 120 °C for 72 h.\cite{64,65} Finally, the GDY powder was dispersed in aqueous solvent under argon atmosphere, and then the aqueous solutions of AgNO$_3$ and sodium citrate were added to the above solution successively. Sodium citrate was used as a reducing agent to reduce AgNO$_3$ to form uniform Ag particles in situ on the surface of GDY. Subsequently, the obtained Ag/GDY powder was loaded onto a carbon cloth and the Ag/GDY/CC cathode electrode was obtained.

Through a scanning electron microscope (SEM) and transmission electron microscope (TEM), the clear micromorphology of Ag/GDY/CC nanomaterials can be accurately obtained. As shown in Figure 1a–d, the spherical silver nanoparticles are uniformly distributed on the surface of GDY. This ordered 2D carbon network of GDY with uniformly distributed micropores serves as a high-quality substrate for the in situ growth of silver nanoparticles. By the direction and restriction of the GDY substrate, the regular-sized AgNPs evenly disperse on it, which prevents the aggregation of the AgNPs. In addition, the high-magnification SEM images reveal that the size of the Ag particles is mostly around 30 nm (Figure 1c). The diameter of the Ag

**Scheme 1.** Schematic diagram for the construction of Ag/GDY nano-electrocatalyst.
particles has been further determined by dynamic light scattering (DLS), which is consistent with the result of high-magnification SEM (the inset of Figure 1d). In addition, TEM images of Ag/GDY/CC with different magnifications before electrocatalysis were captured to characterize the microstructure of the nanomaterial (Figure 1e–g), which suggest that the AgNPs are well dispersed on the surface of 2D GDY nanosheets, and the close contacts have been constructed between AgNPs and GDY. It also suggests that the morphologies of silver particles captured by TEM and SEM are completely consistent. As shown in Figure 1f,g, the high-resolution transmission electron microscope (HRTEM) images capture the Ag (111) plane with 0.23 nm interplanar distances evenly distributed on GDY, which further confirm that the successful loading of uniform AgNPs on the GDY nanosheets enables the exposure of the Ag (111) plane. In addition, the high-angle-annular dark-field (HAADF) image and energy-dispersive X-ray spectroscopy (EDX) elemental mapping for Ag/GDY/CC in Figure 1h–j reveal the spatial distribution of the elements of silver belonging to AgNPs and carbon belonging to GDY in the nanocomposites, which prove the element composition of the catalyst. All these comprehensive and systematic morphology characterization results provide strong support to demonstrate that the special configuration and electron distribution of GDY can fundamentally regulate and activate the AgNPs for electrocatalytic CO₂ reduction.

To verify the construction and chemical composition of the synthesized Ag/GDY/CC nanocomposites, the corresponding powder X-ray diffraction (PXRD), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) measurements were carried out. As shown in Figure 2a, the PXRD diffraction pattern displays five characteristic diffraction peaks at 38.1°, 44.3°, 64.5°, 77.4°, and 81.6°, corresponding to silver (111), (200), (220), (311), and (222) plane (JCPDS no: 87-0717), of which the Ag (111) plane shows the highest intensity, indicating that the combination of AgNPs and GDY can increase the exposure of the Ag (111) plane. The pure GDY shows a wide diffraction peak at 23° in the PXRD diffraction data (Figure 2a, red line), which are well consistent with the diffraction peak of GDY in the in situ-synthesized Ag/GDY/CC nanocomposites (Figure 2a, olive line). In addition, Raman spectroscopy was applied to analyze the microstructure of the sample further. By comparing Figure 2b with Figure 2c, it can be observed that the two characteristic peaks at around 1360 and 1578 cm⁻¹ well correspond to the defined the D and G bands of GDY in the Ag/GDY/CC composites. Meanwhile, the two peaks at 1927 and 2178 cm⁻¹ are in good agreement with the vibration of diacetylene chain in GDY of Ag/GDY/CC composites. In addition, the intensities of the characteristic peaks for Ag/GDY/CC in Figure 2b are much higher than those for pure GDY in Figure 2c, which confirms that the anchoring of silver nanoparticles onto
GDY has a surface-enhanced Raman scattering (SERS) effect on GDY. Therefore, the analysis of Raman spectroscopy moreover proves the successful deposition of silver nanoparticles onto the GDY support and the intimate contact between silver nanoparticles and GDY. In addition, XPS was used to further assess the surface composition and the physical characteristics of the sample. The full XPS spectrum shown in Figure 2d verifies the presence of Ag, C, and O elements in the sample. Here, the appearance of the O element peak at 530 eV can be reasonably assigned to the oxygen in air atmosphere. Figure 2e shows two adjacent peaks with similar intensities located at 367.34 and 373.74 eV that can be attributed to Ag 3d\textsubscript{5/2} and Ag 3d\textsubscript{3/2}, respectively, which reveal the existence of the zero-valance state of Ag nanoparticles in the composites.

Compared with the high-resolution C 1s XPS spectrum of the pure GDY (Figure 2f ii), the XPS of Ag/GDY/CC (Figure 2f i) shows a new peak at 290.12 eV, which is due to the π–π* transitions caused by the restoration of the delocalized conjugated structure, indicating the electronic interaction between the AgNPs and GDY. Based on the earlier analysis, all these results of PXRD, Raman spectrum, and XPS analysis confirm the presence of the strong interactions between the spherical silver nanoparticles and GDY as the uniform AgNPs successfully riveted on GDY sheet, which enables Ag/GDY/CC to be more favorable for electrocatalytic CO\textsubscript{2}RR.

### 2.2. Electrochemical CO\textsubscript{2} Reduction Performance

The prepared Ag/GDY/CC catalyst is subjected to a series of systematic electrochemical measurements in CO\textsubscript{2}-saturated 0.1 M KHCO\textsubscript{3} aqueous solution to evaluate its electrocatalytic activity, selectivity, and stability for CO\textsubscript{2} reduction. Figure 3a shows multiple linear sweep voltammetry (LSV) curves of different materials of CC, GDY/CC, Ag/CC, as well as our synthesized material Ag/GDY/CC for e-CO\textsubscript{2}RR, which were recorded under the same condition from 0 V to −1.6 V versus reversible hydrogen electrode (RHE) (all the following potentials are versus RHE) at the scan rate of 2 mV s\textsuperscript{-1}. Among all these samples, the Ag/GDY/CC nanocomposite has a higher current density than CC, Ag/CC, and GDY/CC at the corresponding potentials. Notably, the current density of the Ag/GDY/CC electrode can reach 57 mA cm\textsuperscript{-2} at −1.6 V. Moreover, the Ag/GDY/CC electrode possesses a much more positive onset potential (∼0.2 V) than that of the other samples. Meanwhile, by comparing the LSV curves of Ag/GDY/CC in argon and carbon dioxide-saturated aqueous solution (the inset of Figure 3a), it can be proved that our prepared material exhibits obvious electrocatalytic reactivity toward CO\textsubscript{2}RR. In addition, the gas- and solution-phase products have been analyzed by gas chromatography (GC) and nuclear magnetic resonance (NMR), respectively. According to the GC analysis, CO and H\textsubscript{2} have been detected and the calculated FEs of CO and H\textsubscript{2} evolution for Ag/GDY/CC and Ag/CC electrodes at different potentials ranging from −1.0 to −1.4 V are shown in Figure 3b. The Faraday efficiency of CO for Ag/GDY/CC can reach a maximum value of 92.1% at −1.3 V, and the maximum value of Ag/CC can only reach the highest value of 72.1% under the same test conditions. Meanwhile, the FEs of H\textsubscript{2} production for the nanocomposite Ag/GDY/CC are below 38% at all the different potentials, whereas the value of Ag/CC can be 78%. Figure S3, Supporting Information, shows the 1\textsuperscript{H} NMR spectrum of the liquid phase, of which all the peaks are attributed to the internal standard solvent dimethyl sulfoxide (DMSO), suggesting no other
CO$_2$ reduction products such as formic acid that evolved in the liquid phase during the electrolysis. Therefore, these analytic data demonstrate that our prepared catalyst Ag/GDY/CC displays very high CO Faraday efficiency and very low H$_2$ Faraday efficiency compared with Ag/CC. Furthermore, the current densities of CO and H$_2$ for Ag/GDY/CC and Ag/CC shown in Figure 3c,d indicate that Ag/GDY/CC exhibits a very high area specific current density up to 25.74 mA cm$^{-2}$ at a potential of –1.3 V for CO evolution, which is more than threefold with respect to that of Ag/CC (7.89 mA cm$^{-2}$); meanwhile, a much lower value of 4 mA cm$^{-2}$ is noticed for the competitive H$_2$ production than that of Ag/CC (6 mA cm$^{-2}$). All of these results reveal that Ag/GDY/CC shows a significant enhancement of electrocatalytic CO$_2$ reduction activity and much more excellent selectivity for CO$_2$ reduction to CO compared with Ag/CC, which could be due to the strong collaborative effect of the Ag nanoparticles and the well-organized GDY confirmed by Raman and XPS spectrum, leading to the cooperative catalytic effect between AgNPs and GDY as well as the increase in catalytically active sites in the composites.

To further investigate the intrinsic origin of the outstanding electrocatalytic properties of our prepared composite Ag/GDY/CC, the electrochemical active surface area (ECSA) and electrochemical impedance spectroscopy (EIS) were conducted. Cyclic voltammetries for Ag/GDY/CC, Ag/CC, and GDY/CC were conducted at different scanning rates of 20–100 mV/s in the non-Faradaic active region (Figure S4, Supporting Information), from which the (ECSA = $C_{dl}$/C$_s$, for carbon cloth, C$_s$ is a constant, and $C_{dl}$ determines ECSA) of different electrodes could be estimated. Figure 3g shows the linear relationship between the scan rates and the current densities of the three kinds of electrodes, which reveals that Ag/GDY/CC has the highest double-layer capacitance ($C_{dl}$) value (12.75 mF cm$^{-2}$), which is 1.6 times than that of Ag/CC and 3 times than that of GDY/CC. Therefore, Ag/GDY/CC possesses the highest ECSA, which establishes that the successful anchoring of the regular-sized AgNPs onto the porous GDY 2D nanosheet can fundamentally regulate and activate the AgNPs and effectively increase the exposure of the maximum Ag surfaces to promote the electrocatalytic activity for e-
In addition, to access the e-CO$_2$RR kinetics of different samples, EIS was recorded in a CO$_2$-saturated 0.1 M KHCO$_3$ aqueous solution and fit to the equivalent circuit model (Figure S4, Supporting Information) with the solution resistance ($R_s$) and the charge transfer resistance ($R_t$). As shown in Figure 3h, Ag/GDY/CC exhibits the smaller solution resistance ($R_s = 2.0 \, \Omega$) and charge transfer resistance ($R_t = 71.4 \, \Omega$) than those of Ag/CC ($R_s = 3.0 \, \Omega$ and $R_t = 158.6 \, \Omega$) and GDY/CC ($R_s = 2.3 \, \Omega$ and $R_t = 3180.1 \, \Omega$). The earlier results suggest that Ag/GDY/CC has the faster electron transfer between the catalyst and electrolyte of the three materials, as well as promotes charge transfer from the catalyst surface to the reactant intermediate COOH$^*$.\[15,19,20,22\]

The HRTEM images in Figure 1f,g confirm the close contacts built between AgNPs and GDY, which provide a basis for the transformation of electrons through the intimate interaction between the phase interface of AgNPs and GDY. In addition, previous studies of GDY composites by Li’s group have proved that the unique high $\pi$-conjugated construction in GDY can facilitate the strong coupling between the $\pi/\sigma^*$ orbitals in the benzene ring ($sp^2$-C) as well as the diacetylenic groups ($sp$-C) of GDY and the $d$ orbital in zero-valence metal, which can result in the rapid electron transfer between the metal atoms and GDY.\[61,66,68\]

Furthermore, compared with the high-resolution C 1$s$ XPS spectrum of the pure GDY (Figure 2f ii), the XPS of Ag/GDY/CC (Figure 2f i) shows a new peak at 290.12 eV, which is due to the $\pi/\pi^*$ transitions caused by the restoration of the delocalized conjugated structure, indicating the electronic interaction between the AgNPs and GDY.\[61,66,67\] In contrast, it can be found from the Raman spectra of Ag/GDY/C (Figure 2b,c) that the characteristic peaks of D band (1360 cm$^{-1}$) and G band (1578 cm$^{-1}$), as well as the vibrations of conjugated diacetylene chain (1927 and 2178 cm$^{-1}$), are all shifted significantly compared with pure GDY. Meanwhile, the intensities of the characteristic peaks for Ag/GDY/CC in Figure 2b in the Raman spectra are much higher than those for pure GDY in Figure 2c, which proves the SERS effect on GDY.\[57\] These results further assure that there is strong electron transfer through the intimate interaction between phase interface of GDY and AgNPs.\[68,69\] Hence, the in situ deposition of AgNPs onto the highly conjugated GDY support with the intimate contact can finely decrease the charge transfer resistance between the phase interface and also highly activate the Ag (111) plane of the AgNPs through the interaction between phase interface electrons, thereby tremendously improving its performance for the electrocatalytic reduction of CO$_2$ to CO.\[14,15\] Furthermore, the electron transfer at the interfaces between the electron-rich GDY and AgNPs can greatly enhance the intrinsic activity of the Ag/GDY/CC composite.\[68,69\]

To study the reaction mechanism of e-CO$_2$RR, density functional theory calculations have been carried out based on three constructed models (Figure 4 and Figure S5, Supporting Information). To explore the active sites and the superior reactivity of our prepared catalyst, we built the three models, Ag (111)/GDY/CC (assuming that the catalysis occurred on the surface of Ag (111)), GDY/Ag (111)/CC (assuming that the catalysis occurred between Ag (111) and GDY), and single Ag (111)/CC, for calculating the free-energy change during electrocatalysis. We tentatively proposed that the catalytic process generally goes through three steps including the generation of the intermediates COOH$^*$ and $^*CO$ and the desorption of CO$_2$.\[28,70\] As shown in Figure 4b,c, at the two applied voltages of 0 and $-1.3 \, V$ versus RHE, the free-energy barriers for the formation of the intermediate products COOH$^*$ and $^*CO$ by Ag (111)/GDY/CC are the lowest of all three models. Moreover, free-energy barriers for the desorption of $^*CO$ to CO$_2$ on Ag (111)/GDY/CC and Ag (111)/CC are also the lowest. Therefore, the results suggest that Ag (111)/GDY/CC has higher electrocatalytic activity than GDY/Ag (111)/CC and Ag (111)/CC. Due to the transformation of electrons between the phase interface of GDY and AgNPs induced by strong coupling between the $\pi/\pi^*$ orbitals in $sp^2$-C

![Figure 4](https://www.advancedsciencenews.com)

Figure 4. a) Calculation models for different materials. Free-energy diagrams for CO$_2$RR to CO on different facets at b) 0 V versus RHE and c) $-1.3 \, V$ versus RHE.
as well as sp-C of GDY and the d orbital in zero-valence metal, the required free-energy barrier for the formation of the intermediates COOH* and *CO on Ag (111)/GDY/CC is 0.3 eV/0.3 eV lower than the single Ag particle. All the experimental and theoretical results reveal that the electron transfer between the interface of GDY and AgNPs may enable the surface of the catalyst with high electron density to facilitate the formation of the COOH* and *CO intermediates, together with the desorption of CO, which can remarkably improve the e-CO₂RR reactivity of the Ag/GDY/CC.[61,69,71,72]

The stability of the electrocatalyst is of great importance in electrocatalyzing CO₂RR. To explore the durability of the composites, electrolysis was conducted with the two materials Ag/GDY/CC and Ag/CC in CO₂-saturated 0.1 m KHCO₃ aqueous solution. The current–time (I–t) curves of Ag/GDY/CC and Ag/CC shown in Figure 3e show that Ag/GDY/CC keeps a much higher current density of 25.74 mA cm⁻² unchanged during 24 h of electrolysis at the controlled potential of −1.3 V, whereas Ag/CC exhibits a much smaller current density at around 8 mA cm⁻² with a downward trend, which indicates that the Ag/GDY/CC electrode displays much higher stability for catalytic CO₂ reduction to CO. Figure 3f also shows the electrocatalytic stability of Ag/GDY/CC, which reveals that there is almost negligible degradation of current density after 2000 cycles tests, confirming the excellent stability of our prepared electrode for e-CO₂RR. In addition, to further ensure the stability of Ag/GDY/CC composite after electrocatalysis, the corresponding SEM, DLS, HRTEM, PXRD, Raman, and XPS after electrocatalysis were also studied. Figure S1a, Supporting Information, shows the TEM and DLS of Ag/GDY/CC composite after electrocatalysis, which fully prove that the morphology of the catalyst after the reaction does not change, and the diameter of silver particles is close to that before electrocatalysis. The HRTEM image in Figure S1b, Supporting Information, clearly captures the Ag (111) plane of the nanoparticle, which is completely consistent with that in Figure 1f,g further confirming the uniform distribution of silver nanoparticles on the GDY after electrocatalysis. Figure S1c–e, Supporting Information, also correspondingly shows that the element distribution of the catalyst does not change after long-time electrocatalytic reaction. By comparison, the comprehensive and systematic HRTEM images of Ag/GDY/CC after the electrocatalytic reaction confirm that the material retains its initial silver particle structure and the Ag (111) plane, which strongly supports the great stability of the catalyst. In addition, the PXRD test results (Figure S2a, Supporting Information) after electrocatalysis are consistent with those before electrocatalysis (Figure 2a). In addition, the Raman spectroscopy in Figure S2b, Supporting Information, further proves the high stability of Ag/GDY/CC catalyst, in which the GDY SERS produced by the in situ growth of Ag particles on the GDY nanosheet is again observed after catalysis. Figure S2c–e, Supporting Information, shows the XPS survey of Ag/GDY/CC, in which the high-resolution XPS spectra of Ag 3d and C 1s spectra of Ag/GDY/CC after electrocatalysis are similar to those before catalysis, respectively. All these analytic results fully confirmed that the combination of Ag nanoparticles with GDY significantly improved the stability of the material. By the direction and restriction of the GDY template, the effective in situ loading of the ordered AgNPs on it can not only prevent the aggregation of AgNPs, but also highly stabilize the AgNPs, which leads to the superior stability of the Ag/GDY/CC composite.[40] All these results also confirm that with the stabilization of GDY, the oxidation state of Ag cannot increase. In contrast, the transformation of electrons between the phase interface of GDY and AgNPs should be through the strong coupling between the π*π* orbitals of GDY and the d orbital in Ag; meanwhile, the charge occupation can be mutually compensated via the band overlapping between C-(2s 2p) orbital of GDY and d orbital of Ag atom; thus, the oxidation state of Ag should be stable.[61,66,68]

3. Conclusion
In summary, a novel e-CO₂RR catalyst Ag/GDY/CC has been designed and prepared by simple in situ synthesis method on the basis of GDY. The direct anchoring of AgNPs onto the highly conjugated GDY template with the intimate contact can improve the exposure of the maximum Ag surfaces and highly activate the Ag (111) plane of the AgNPs via the interaction between phase interfaces, therefore enhancing the charge transfer and effectively promoting its electrocatalytic activity for reduction of CO₂ to CO with a high Faraday efficiency of 92.1% and a high current density of 25.74 mA cm⁻². In contrast, through the direction and restriction of the GDY support, the strong combination along with cooperation of AgNPs and GDY can prevent the accumulation of the AgNPs and further extremely stabilize the AgNPs, resulting in the great stability of the Ag/GDY/CC composite with up to 24 h long-term durability. In this case, our finding of the GDY functional composite opens up a new avenue to design and synthesize efficient electrocatalysts for practical selective reduction of CO₂.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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