

## Electrocatalysis

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## Engineering the Coordination Environment of Single-Atom Platinum Anchored on Graphdiyne for Optimizing Electrocatalytic Hydrogen Evolution

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Abstract: Two Pt single-atom catalysts (SACs) of Pt-GDY1 and Pt-GDY2 were prepared on graphdiyne (GDY)supports. The isolated Pt atoms are dispersed on GDY through the coordination interactions between Pt atoms and alkynyl C atoms in GDY, with the formation of five-coordinated  $C_1$ -Pt-Cl<sub>4</sub> species in Pt-GDY1 and four-coordinated C<sub>2</sub>-Pt-Cl<sub>2</sub> species in Pt-GDY2. Pt-GDY2 shows exceptionally high catalytic activity for the hydrogen evolution reaction (HER), with a mass activity up to 3.3 and 26.9 times more active than Pt-GDY1 and the state-of-the-art commercial Pt/C catalysts, respectively. Pt-GDY2 possesses higher total unoccupied density of states of Pt 5d orbital and close to zero value of Gibbs free energy of the hydrogen adsorption  $(|\Delta G_{H^*}^{Pt}|)$  at the Pt active sites, which are responsible for its excellent catalytic performance. This work can help better understand the structure-catalytic activity relationship in Pt SACs.

he hydrogen evolution reaction (HER) through electrocatalytic water splitting is considered a promising approach for the production of clean hydrogen, which has been regarded as one of the most potential energy carriers in the future.<sup>[1-3]</sup> Among the developed electrocatalysts, Pt-based catalysts are the most effective electrocatalysts for HER.<sup>[4-6]</sup> However, the scarcity and high cost of noble-metal Pt limit their large-scale applications. Notably, the platinum utilization in traditional Pt-based catalysts is very low, as the active sites only come from Pt atoms on the surface of the catalysts. Therefore, great efforts have been devoted to increase the platinum utilization as well as to improve the HER activity of Pt-based catalysts.<sup>[7,8]</sup> Compared with traditional Pt-based catalysts, Pt single-atom catalysts (SACs) have great advant-

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For SACs, the coordination environments of metal atoms will greatly influence their electronic structures, and subsequently affect their catalytic activity.<sup>[16]</sup> For example, Zhang et al. found that Fe<sup>III</sup>N<sub>5</sub> species in Fe SACs displays the highest catalytic activity for selective oxidation of the C-H bond, which is one order magnitude more active than  $Fe^{III}N_6$ species and three times more active than Fe<sup>II</sup>N<sub>4</sub> species.<sup>[17]</sup> Wu and co-workers constructed a series of Co SACs with different nitrogen coordination numbers, and they found that atomically dispersed Co with two coordinate nitrogen atoms displays the best CO2 electroreduction catalytic performance.<sup>[18]</sup> Though the coordination environments of metal atoms are closely related to their catalytic activity in SACs, there is rare investigation for the influence of Pt atoms coordination environments on their catalytic activity of HER in Pt SACs. To better understand the structure-activity relationship between the coordination environment of Pt atoms and the corresponding HER catalytic activity in Pt SACs, it is imperative to disperse the individual Pt atoms on a stable support with adjustable coordination environments.

Herein, we put forward a simple method for the synthesis of two Pt SACs on the support of graphdiyne (GDY). As a new man-made carbon allotrope, GDY possesses of uniform 18 C-hexagonal pores formed by three butadiyne linkages (- $C \equiv C - C \equiv C^{-}$ ) between the benzene rings (see Figure 1),<sup>[19-21]</sup> which can provide ideal anchoring sites for single Pt atoms with high stability, as demonstrated by the results of theoretical calculations.<sup>[22a]</sup> More recently, zero valence Ni and Fe single atoms anchored on the pores of GDY for hydrogen evolution has been reported.[22b] Based on the unique structure of GDY, we constructed two Pt SACs simply by the reaction of GDY with K<sub>2</sub>PtCl<sub>4</sub> aqueous solution at 273 K for 8 h (named as Pt-GDY1), and subsequently annealing in Ar atmosphere at 473 K for 1 h (named as Pt-GDY2). The results of atomic resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and X-ray absorption fine structure



Figure 1. Illustration for the synthesis of Pt-GDY1 and Pt-GDY2.

(XAFS) spectra in *R* space, as well as the first-principles calculations verify that the isolated Pt atoms are anchored on the surface of GDY by the coordination interactions of Pt with the alkynyl C atoms in GDY, forming a five-coordinated C<sub>1</sub>-Pt-Cl<sub>4</sub> species and a four-coordinated C<sub>2</sub>-Pt-Cl<sub>2</sub> species in Pt-GDY1 and Pt-GDY2, respectively. Interestingly, Pt-GDY2 shows much higher HER catalytic activity than Pt-GDY1 and commercial Pt/C, with a mass activity up to 3.3 times and 26.9 times more active than Pt-GDY1 and Pt/C catalysts, respectively. The higher HER catalytic activity of Pt-GDY2 originates from its higher total unoccupied density of states of Pt 5d orbital and close to zero  $|\Delta G_{H^*}^{Pt}|$  value.

Atomically dispersed Pt species were anchored on GDY by a wet-chemical route as shown in Figure 1. First, graphdivne was synthesized and grown on the titanium foils by a modified Hay-Glaser coupling reaction using hexaethynylbenzene as a precursor.<sup>[23]</sup> The sp-hybridized alkynyl carbon atoms in the 18 C-hexagonal pores in GDY provide ideal anchoring sites for immobilizing the isolated Pt atoms into the GDY framework. In the wet-chemical approach, K<sub>2</sub>PtCl<sub>4</sub> was used as a precursor and reacted with GDY at 273 K for 8 hours to generate the Pt-GDY1 sample. The Pt-GDY2 sample was obtained by annealing Pt-GDY1 at 473 K under Ar atmosphere for 1 h. Notably, Pt-GDY1 and Pt-GDY2 maintain the morphology of GDY with no obvious Pt clusters formed, as shown in the SEM and TEM images in the Supporting Information, Figure S1. Furthermore, the XRD patterns for Pt-GDY1 and Pt-GDY2 also demonstrate that no Pt nanoparticles formed in two Pt SACs (Supporting Information, Figure S2).

The abundant isolated Pt atoms on GDY support can be verified by the HADDF-STEM images. As shown in Figures 2a and b, the HADDF-STEM images for both Pt-GDY1 and Pt-GDY2 display isolated bright dots, which can be attributable to the heavy Pt atoms. Furthermore, the elemental mapping images for Pt-GDY2 reveal the homogeneous spatial distributions of carbon, platinum and chlorine on GDY (Figure 2c). The energy dispersive spectroscopy (EDS) measurement (Figure 2d) confirms the presence of C, Pt, and Cl elements in Pt-GDY2 (other elements derived from Cu grid). The above results demonstrate that abundant single Pt atoms are successfully dispersed on GDY support in Pt-GDY1 and Pt-GDY2. Furthermore, the Pt loading in both Pt-GDY1 and Pt-GDY2 were measured using inductively coupled plasma-atomic emission spectroscopy (ICP-AES), with a Pt loading of 4.65  $\mu$ g cm<sup>-2</sup> for both Pt-GDY1 and Pt-



*Figure 2.* a),b) Atomic-resolution HAADF-STEM images for Pt-GDY1 (a) and Pt-GDY2 (b). c) Elemental mapping for Pt-GDY2. d) The EDS for Pt-GDY2.

GDY2, indicating the Pt atoms anchored on GDY are not lost during the annealing process.

The compositions of Pt-GDY1 and Pt-GDY2 were investigated by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). As shown in Figure 3a, the Raman spectrum of as-synthesized GDY shows distinct four peaks at 1384.2, 1572.9, 1926.4, and 2181.4 cm<sup>-1</sup>, respectively, which is consistent with the reported values,<sup>[24]</sup> in which the peak at 1384.2 cm<sup>-1</sup> is due to the breathing vibration of sp<sup>2</sup> carbon domains in aromatic rings (D band), the peak at 1572.9 cm<sup>-1</sup> corresponds to the first-order scattering of the  $E_{2g}$  mode for in-phase stretching vibration of sp<sup>2</sup> carbon domains in



**Figure 3.** a) Raman spectra of GDY, Pt-GDY1, and Pt-GDY2. b) Highresolution core level spectra of Pt 4f for Pt-GDY1, Pt-GDY2, and  $K_2$ PtCl<sub>4</sub>. c) Pt L<sub>3</sub>-edge XANES spectra of Pt-GDY1, Pt-GDY2, and Pt foil. Inset: enlarged spectra at Pt L<sub>3</sub>-edge. d) Pt L<sub>3</sub>-edge k<sup>3</sup>-weighted FT-EXAFS spectra of Pt-GDY1, Pt-GDY2, and Pt foil (the EXAFS intensity of Pt foil is shown at half value).

aromatic rings (G band), and the peaks at 1926.4 and 2181.4 cm<sup>-1</sup> can be attributed to the vibration of conjugated diyne linkers. After the formation of Pt-GDY1 and Pt-GDY2, their G bands have a hypsochromic shift compared to that of GDY, and the intensities belonging to the conjugated diyne linkers become weaker (Figure 3 a), indicating the formation of coordination bonds between the single Pt species and the carbon atoms of conjugated diyne linkers in GDY.<sup>[25]</sup>

The valence states of isolated Pt atoms in Pt-GDY1 and Pt-GDY2 were investigated by XPS. As shown in Figure 3b, the high-resolution core level spectra of Pt 4f in Pt-GDY1, Pt-GDY2 and  $K_2PtCl_4$  display  $4f_{7/2}$  and  $4f_{5/2}$  doublets owing to the spin–orbital splitting. The Pt  $4_{\rm f7/2}$  and  $4f_{\rm 5/2}$  of  $K_2PtCl_4$  locate at 73.0 and 76.3 eV, respectively, which are consistent with the values of Pt<sup>2+</sup> as reported in the literatures.<sup>[26]</sup> While the peaks of Pt  $4f_{7/2}$  and  $4f_{5/2}$  in Pt-GDY1 and Pt-GDY2 shift to lower binding energy relative to those of K<sub>2</sub>PtCl<sub>4</sub>, indicating the electron transfers from the alkynyl C atoms in GDY to Pt atoms after the formation of Pt-GDY1 and Pt-GDY2.[27] Furthermore, the Pt  $4f_{7/2}$  and  $4f_{5/2}$  peaks at 72.8 and 76.0 eV in Pt-GDY2 are slightly larger than the corresponding values of 72.6 and 75.8 eV in Pt-GDY1, indicating the Pt atoms in Pt-GDY2 have a higher valence state than those in Pt-GDY1. The above results further demonstrate the formation of coordination bonds between the Pt atoms and the conjugated alkynyl C atoms of GDY in Pt-GDY1 and Pt-GDY2, and the Pt atoms in Pt-GDY2 possess of more positive valence state than those in Pt-GDY1.

To further investigate the electronic structure and coordination environments of single Pt atoms in Pt-GDY1 and Pt-GDY2, the Pt L<sub>3</sub>-edge X-ray absorption near edge structure (XANES) and extended X-ray fine structure (EXAFS) were studied. As shown in Figure 3c, the XANES spectra of Pt-GDY1 and Pt-GDY2 are much different from that of Pt foil, as the Pt atoms in Pt-GDY1 and Pt-GDY2 are individually dispersed on GDY.<sup>[28]</sup> Furthermore, the L<sub>3</sub>-edge white-line (WL) intensities increase in an order of Pt foil < Pt-GDY1 < Pt-GDY2 (inset in Figure 3c). The increase in the WL intensity means a decrease in the number of electrons in the d orbital.<sup>[13]</sup> To further understand the unoccupied density of states of Pt 5d orbital, quantitative WL intensity of Pt-GDY2, Pt-GDY1 and Pt foil were conducted by the reported methods.<sup>[29]</sup> As shown in the Supporting Information, Figure S3 and Table S1, Pt-GDY2 has the highest total unoccupied density states of Pt 5d character, while metal Pt has the lowest. As is well known, the vacant d orbitals of the isolated atoms play an important role during the catalytic process, and are responsible for the outstanding catalytic activity of SACs.[13]

The Fourier transformations (FT) of  $k^3$ -weighted for EXAFS oscillations for Pt-GDY1, Pt-GDY2, and Pt foil are shown in Figure 3 d. The Pt foil exhibits a strong peak at about 2.8 Å, which is ascribed to the Pt–Pt bond. In the FT-EXAFS of Pt-GDY1 and Pt-GDY2, only the peaks in the distances of 1.9–2.3 Å were observed, while no Pt–Pt contribution was found, further confirming that Pt has been atomically dispersed on the surface of GDY in Pt-GDY1 and Pt-GDY2 from macroscopic view, being consistent with the observations of HADDF-STEM images in microdomain. The two

peaks at about 1.9 and 2.3 Å in the FT-EXAFS curves for Pt-GDY1 and Pt-GDY2 are associated with Pt-C and Pt-Cl bonds, respectively, and the corresponding intensities of Pt-C and Pt-Cl in R-space for Pt-GDY1 and Pt-GDY2 are given in the Supporting Information, Figure S4. To obtain the coordination environment around Pt, the FT-EXAFS curves of Pt-GDY1 and Pt-GDY2 were fitted in R space. The fitting results indicate that the Pt atoms anchored on GDY by coordinating with one carbon and four chlorine atoms in Pt-GDY1, and two carbon and two chlorine atoms in Pt-GDY2 (Supporting Information, Table S2). The fitting curves accord well with the experimental curves in R and k space, respectively (Supporting Information, Figures S5 and S6), demonstrating the accurate simulation for the coordination environments of Pt atoms in Pt-GDY1 (C1-Pt-Cl4) and Pt-GDY2 (C2-Pt-Cl2). Furthermore, the adsorption energy ( $\Delta E_{ads}$ ) of these two kinds of isolated Pt species on the surface of GDY was calculated by the first-principles calculations. As shown in the Supporting Information, Figure S7, the  $\Delta E_{ads}$  is -0.183 eV for Pt-GDY1 and -1.142 eV for Pt-GDY2, indicating both the reactions of [PtCl<sub>4</sub>]<sup>2-</sup> and PtCl<sub>2</sub> species with the alkynyl carbons of GDY are thermal favorable, and Pt-GDY2 is more stable than Pt-GDY1.

To understand the effect of coordination environments of Pt in SACs on their HER catalytic activity, we investigated the electrocatalytic performance of Pt-GDY1 and Pt-GDY2 in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution with a three-electrode setup. In the meanwhile, commercial Pt/C catalyst was used to evaluate the HER catalytic activity of Pt-GDY1 and Pt-GDY2. As shown in the Supporting Information, Figure S8a, Pt-GDY2 shows much better HER catalytic activity than Pt-GDY1 and commercial Pt/C catalyst at an overpotential larger than -0.05 V. To rationally compare the catalytic performance, their HER catalytic activity was normalized to the current/Pt loading mass  $(Amg^{-1})$ . As shown in Figure 4a, the polarization curves for Pt-GDY1, Pt-GDY2, and commercial Pt/C were recorded from linear sweep voltammetry (LSV) measurements, with a scan rate of  $5 \text{ mV s}^{-1}$  at room temperature. Notably, Pt-GDY2 displays much higher HER catalytic activity than Pt-GDY1 and commercial Pt/C catalysts. As shown in Figure 4b, the mass activities for Pt-GDY2, Pt-GDY1, and Pt/C at an overpotential of 100 mV are 23.64, 7.26, and 0.88 A mg<sup>-1</sup>, respectively, in which Pt-GDY2 shows 26.9 and 3.3 times more active than Pt/C and Pt-GDY1 catalysts, respectively. Moreover, Pt-GDY2 catalyst achieved a Tafel slope of 46.6 mV/dec, much smaller than those of Pt-GDY1 (52.0 mV/dec) and Pt/C (127.5 mV/dec), as exhibited in Figure 4c.

The long-term CV cycling test and time-dependent current density curve were tested to examine the stability of Pt-GDY2 catalyst. The polarization curve of Pt-GDY2 after 1000 cycles maintains similar as the initial curve (Figure 4d). The time-dependent current density curve at -95 mV for 10000 s also confirms the superior stability of Pt-GDY2 (inset in Figure 4d). The platinum contents in Pt-GDY2 before and after HER test are almost the same (Supporting Information, Table S3), indicating no Pt atoms lost during the catalytic process. Furthermore, the results of atomic-resolution HAADF-STEM image (Supporting Information, Figure S9),



**Figure 4.** a) The polarization curves for Pt-GDY1, Pt-GDY2, and commercial Pt/C in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, with a scan rate of 5 mVs<sup>-1</sup>. b) The HER mass activity at  $\eta = -0.1$  V for Pt/C, Pt-GDY1, and Pt-GDY2. c) Tafel plots of Pt/C, Pt-GDY1, and Pt-GDY2 for HER. d) Durability measurements for Pt-GDY2 SAC. The polarization curves of Pt-GDY2 at initial and after 1000 cycles with a scan rate of 5 mVs<sup>-1</sup> (Inset: the time-dependent current density curve at -95 mV vs. RHE for 10000 s).

XANES and FT-EXAFS spectra (Supporting Information, Figure S10) measurements for Pt-GDY2 after the HER test indicate the Pt atoms still keep individual dispersion as those in pristine Pt-GDY2, suggesting its excellent stability. To eliminate the effect from the Pt counter electrode, graphite rod was also used to instead of Pt wire as the counter electrode for the HER test. As shown in the Supporting Information, Figures S8d,e, the polarization curves and the time-dependent current density curves for Pt-GDY2 by using the graphite rod as the counter electrode are the similar to those of Pt-GDY2 by using the Pt wire as the counter electrode. The above results suggest that Pt SACs dispersed on GDY can efficiently enhance the Pt utilization as well as the catalytic activity for HER, compared with Pt nanoparticles counterpart of commercial Pt/C. And the Pt atoms in Pt-GDY2 with a C2-Pt-Cl2 coordination environment show much higher HER catalytic activity than the Pt atoms in Pt-GDY1 with a C<sub>1</sub>-Pt-Cl<sub>4</sub> coordination environment.

To better understand the origin of the enhanced HER catalytic activity of Pt-GDY2, the Gibbs free energy for hydrogen adsorption ( $\Delta G_{\text{H}^*}$ ) on GDY, Pt-GDY1 and Pt-GDY2 were calculated (Figure 5; Supporting Information, Figure S11). As is well-known,  $\Delta G_{\text{H}^*}$  is an important descriptor for the HER catalytic activity of different catalysts, which is usually proposed to have an optimal value being close to zero.<sup>[30,31]</sup> On the one hand, the  $\Delta G_{\text{H}^*}$  for pure GDY (0.801 eV) is too positive, implying that H cannot be efficiently adsorbed on the surface of GDY, and its HER catalytic activity is impeded. On the other hand, the  $\Delta G_{\text{H}^*}^{\text{Pt}}$  for Pt-GDY1 (-0.653 eV) is too negative, indicating the adsorption of H on the Pt active site in Pt-GDY1 is too strong, which is also unfavorable for HER process. For Pt-GDY2, the  $\Delta G_{\text{H}^*}^{\text{Pt}}$  is 0.092 eV, which is close to that on the surface of Pt metal



*Figure 5.* a) The configuration of Pt-GDY2 with hydrogen adsorbed on. b) The calculated Gibbs free energy diagram for hydrogen evolution on different catalysts.

 $(\Delta G_{\rm H^{*}}^{\rm Pt} \approx -0.09 \text{ eV})$ ,<sup>[32]</sup> indicating its excellent HER catalytic activity originates from its optimal  $\Delta G_{\mathrm{H}^*}^{\mathrm{Pt}}$  value for the adsorption of H on the individual Pt active site anchored on GDY with a C<sub>2</sub>-Pt-Cl<sub>2</sub> coordination environment. Additionally, the total unoccupied density of states of Pt 5d orbital has been proven to be closely related to the hydride formation.<sup>[13]</sup> as Pt 5d orbital could interact with the 1s orbital of H atom, benefiting to transfer electrons to H atom. The total unoccupied density of states of Pt 5d character increases in an order of Pt metal < Pt-GDY1 < Pt-GDY2, as obtained from the results of XANES analysis (Supporting Information, Table S2). This brings about the exclusive electronic structure of the isolated Pt atoms with a C2-Pt-Cl2 coordination environment on GDY, which contributes to its excellent HER activity. Though Pt-GDY1 has a large negative  $\Delta G_{H^*}^{Pt}$ value of -0.653 eV, it still has a higher mass activity than commercial Pt/C due to its utmost Pt utilization. Overall, the appropriate  $|\Delta G_{\rm H}^{\rm Pt}|$  value and higher unoccupied 5d densities of states of Pt atoms in Pt-GDY2 are responsible for its optimal HER catalytic activity.

In conclusion, a facile method was reported for the synthesis of two Pt SACs of Pt-GDY1 and Pt-GDY2 with different Pt coordination environments. It has shown that the coordination environments of Pt atoms in Pt SACs greatly affect their HER catalytic activity, in which Pt-GDY2 SAC with four coordinated Pt atoms of C2-Pt-Cl2 shows the highest HER catalytic performance. The outstanding HER catalytic activity of Pt-GDY2 originates from its near to zero  $|\Delta G_{H^*}^{Pt}|$ value of 0.092 eV on four-coordinated Pt atom, as well as its higher unoccupied density of states of Pt 5d orbital. Our results demonstrate that GDY may serve as an ideal support for the design and synthesis of other stable noble metal SACs due to its unique structure, in which the isolated noble metal such as Pt can be easily anchored on the surface of GDY by the strong coordination interactions of noble metal with the alkynyl C atoms in GDY. In the next step, we will try to construct other noble metal SACs using GDY as a support and investigate their unique catalytic properties.

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## Conflict of interest

The authors declare no conflict of interest.

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