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Nano Res., **Just Accepted Manuscript** • <https://doi.org/10.26599/NR.2026.94909196>

<https://www.sciopen.com/journal/1998-0124> on Sep. 17, 2026

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 **Cite this article:** *Nano Research*, 2026, 19, 94909196 <https://doi.org/10.26599/NR.2026.94909196>

ABSTRACT: Modulating the electronic structure of supported metal nanoparticles through rational catalyst design has emerged as an effective strategy for enhancing electrocatalytic performance, yet the interplay between metal nanoparticles and carbon supports in boosting reactive oxygen species (ROS) electrosynthesis remains poorly understood. Here, we report a strategy to achieve highly efficient ROS electrosynthesis with graphdiyne (GDY)-supported palladium-platinum nanoparticles (PdPt/GDY) as the catalyst. PdPt/GDY is prepared by successive electroless deposition of Pd and Pt. With the PdPt/GDY as the catalyst, the electrochemical synthetic system produces substantially more ROS from hydrogen peroxide (H₂O₂) reduction reaction (HPRR) compared with those with PdPt nanoparticles supported onto other carbon-based nanomaterials as the catalysts. Operando luminol electrochemiluminescence (ECL) characterization and theoretical calculation reveal the origin of the high efficiency for ROS synthesis, which stems from the synergistic Pd-Pt atomic interactions and strong coupling of metal nanoparticles with alkyne-rich GDY. The high efficiency of PdPt/GDY for ROS electrosynthesis enables superior perfluorooctanoic acid degradation and defluorination among all carbon-supported PdPt analogues, highlighting its high capability for the deep degradation of persistent fluorinated pollutants. This work establishes a framework for rational catalyst design for sustainable ROS electrosynthesis with appealing environmental applications.

KEYWORDS: electrosynthesis, reactive oxygen species, graphdiyne, operando analysis, perfluorooctanoic acid degradation

1. Introduction

Substrate-supported noble metal nanoparticles represent a major class of catalysts [1-9] because the substrate not only stabilizes the metals to prevent aggregation but also modulates the interfacial charge transfer through electron coupling [10], geometric confinement [11], and structural/electronic interactions [12]. Among the carbon substrates reported so far [10, 13-14], graphdiyne (GDY) has attracted increasing attention because of its unique alkyne-rich and π -conjugated structure that provides abundant coordination sites and promotes strong electronic coupling at the metal-support interface [3-4, 8, 15-21]. We recently found that electroless deposition of Pd nanoparticles on GDY substrate enables strong electronic metal-support interaction (EMSI), which can induce interfacial charge redistribution and modulate the d-band electronic structure of Pd, thereby promoting efficient reactive oxygen species (ROS) generation and stable accumulation [15].

ROS, such as hydroxyl radicals ($\cdot\text{OH}$) and superoxide ($\text{O}_2^{\cdot-}$), are powerful oxidants that drive key processes in catalysis, biomedicine, and environmental remediation [16, 18-22]. ROS synthesis via electrocatalytic oxygen reduction reaction

(ORR) or hydrogen peroxide reduction reaction (HPRR) has therefore emerged as a transformative research frontier, offering precisely controllable and sustainable ROS synthesis through renewable energy-driven processes, bridging disciplines from electrosynthesis to biomedical and environmental engineering [23-25]. ROS electrosynthesis not only drives fundamental breakthroughs in synthetic chemistry but also provides critical insights into physiological and disease mechanisms [26-29]. Furthermore, ROS synthesis enables advanced environmental remediation technologies through efficient pollutant degradation [30] and microbial inactivation [31]. Nevertheless, the ROS generation efficiency remains low.

Alloying is an effective strategy for tuning the d-band electronic structure of metal catalysts, thereby modulating the adsorption behavior of oxygen-containing intermediates and the interfacial reaction kinetics, as reported previously [32]. Thus, we speculate that introducing Pt, which possess strong H₂O₂/O₂ activation capability [33], into Pd/GDY could achieve synergistic electronic regulation through alloying effect and EMSI. Specifically, Pd-Pt alloying is expected to optimize the d-band electronic structure of the metal sites, thereby regulating the generation, conversion, and

desorption of key oxygen-containing intermediates during ROS electrosynthesis. Meanwhile, the EMSI between Pd-Pt and GDY could induce interfacial charge redistribution, further optimizing the electronic structure of the bimetallic system. Such dual synergistic regulation is expected to improve interfacial electron transfer and ROS generation kinetics, ultimately enhancing ROS electrosynthesis performance.

Here, we design PdPt/GDY through electroless deposition of palladium-platinum nanoparticles on graphdiyne for highly efficient ROS electrosynthesis, with luminol electrochemiluminescence (ECL) as the operando method for ROS monitoring, since ROS can trigger the chemiluminescence of luminol immediately with

exceptionally high sensitivity because of its near-zero background [34-37]. We find that the efficiency of the PdPt/GDY-based ROS electrosynthesis outperforms those with the catalysts including disparate carbon-based Pd-Pt nanocomposites and PdPt/GDY with various Pd-Pt ratios. Mechanistic studies reveal that the synergistic interaction between Pd and Pt as well as the strong EMSI between PdPt nanoparticles and GDY substrate together contribute to the highly efficient ROS electrosynthesis. Encouraged by these results, we further apply the system for perfluorooctanoic acid (PFOA) degradation, where PdPt/GDY features the highest PFOA removal efficiency and defluorination ratio among the catalysts examined, outperforming PdPt/GO, PdPt/MCNT, and PdPt/GR. These findings highlight the potential of rationally engineered catalyst systems for efficient ROS electrosynthesis and pollutant degradation.

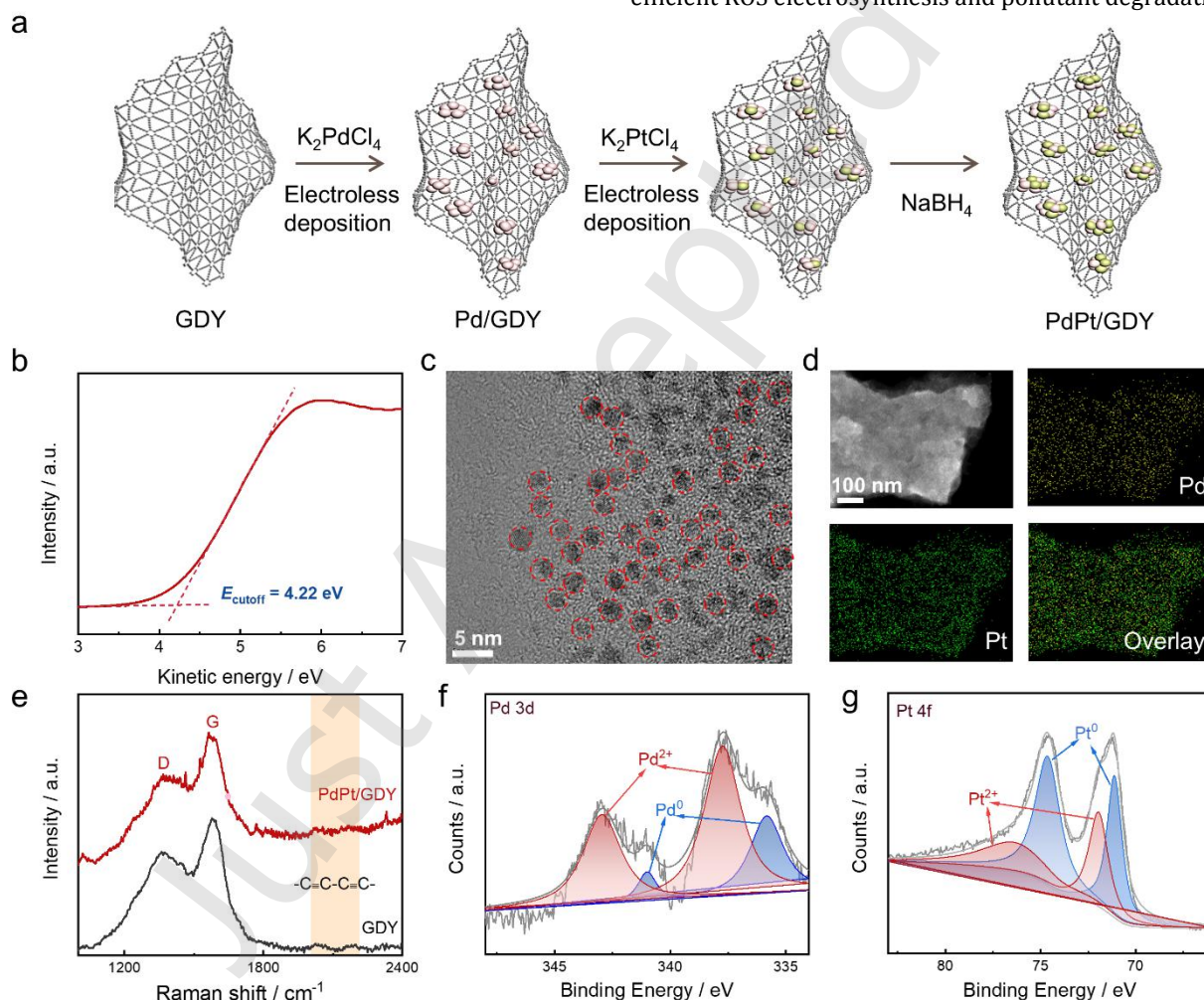


Figure 1. Synthesis and characterization of PdPt/GDY. (a) Illustration of the PdPt/GDY formation via electroless deposition and chemical reduction. (b) UPS spectra of Pd/GDY. (c) HRTEM image of PdPt/GDY. (d) EDS elemental mappings of PdPt/GDY: Pd (yellow), and Pt (green). (e) Raman spectra of GDY and PdPt/GDY. High-resolution XPS of (f) Pd 3d and (g) Pt 4f.

2. Results and discussion

2.1 Synthesis and characterization of PdPt/GDY catalyst.

To synthesize the PdPt/GDY catalyst, we employed sequential electroless deposition method followed by brief chemical reduction (Fig. 1a). In this process, GDY serves as both a substrate and an electron donor. The reduction potential of GDY (-0.33 V vs. SHE) is more negative than those of PdCl_4^{2-} (+0.62 V vs. SHE) and PtCl_4^{2-} (+0.78 V vs.

SHE) [15, 28, 38], providing the possibility to successive reduction of both metal precursors. Pd was first electroless-deposited on GDY by mixing GDY with PdCl_4^{2-} , yielding Pd/GDY with a reduction potential of -0.08 V vs. SHE (Fig. 1b). This reduction potential remains sufficiently low to enable the further reduction of PtCl_4^{2-} , allowing for the subsequent deposition of Pt on the Pd/GDY in the same procedure. Then, we mixed Pd/GDY with PtCl_4^{2-} for 30 min to form PdPt/GDY, and NaBH_4 was subsequently added to

the PdPt/GDY dispersion to ensure complete reduction of metal precursors and form PdPt nanoparticles [39-40]. Scanning electron microscope (SEM) image shows that the PdPt/GDY exhibits a multilayered lamellar structure (Fig. S1a), and high-resolution transmission electron microscopy (HRTEM) reveals that the nanoparticles with an average size of 2.1 nm are uniformly (Fig. 1c and Fig. S2). The uniform elemental distribution of Pd and Pt across the GDY nanosheets is also corroborated by the elemental mapping (Fig. 1d and Fig. S1b). Energy dispersive spectra (EDS) show the successful loading of PdPt nanoparticles onto GDY (Fig. S1c and S1d), in which Pd and Pt are co-doped in a disordered atomic arrangement as observed with the elemental mapping overlay image (Fig. 1d).

Raman and X-ray photoelectron spectroscopy (XPS) of the PdPt/GDY were performed to gain a better insight into the electronic structure and the interfacial electronic interactions between PdPt and GDY. As shown in Fig. 1e, the Raman spectra of the PdPt/GDY show the attenuation of the characteristic bands for $\text{-C}\equiv\text{C-C}\equiv\text{C-}$ at 2025 cm^{-1} and 2188 cm^{-1} and small shifts in the D/G ratio relative to pristine GDY, suggesting the charge transfer at the interface between metals and GDY. [41-42] XPS profile analysis confirms the presence of Pd and Pt peaks of the PdPt/GDY (Fig. S3a), consistent with the EDS analysis (Fig. 1d). In Fig. 1f, the binding energy values at 335.80 and 341.20 eV respectively correspond to $\text{Pd}^0\ 3d_{5/2}$ and $\text{Pd}^0\ 3d_{3/2}$, and 337.70 eV and 342.90 eV were attributed to $\text{Pd}^{2+}\ 3d_{5/2}$ and $\text{Pd}^{2+}\ 3d_{3/2}$, respectively. The Pt 4f spectrum of the PdPt/GDY was deconvoluted into four peaks at 71.40, 74.60, 71.90, and 76.30 eV, which were ascribed to $\text{Pt}\ 4f_{7/2}$ and $\text{Pt}\ 4f_{5/2}$ of Pt^0 and Pt^{2+} (Fig. 1g), respectively. The binding energies of $\text{Pt}^0\ 4f$ and $\text{Pd}^0\ 3d$ are slightly different from the standard values of bulk Pt ($4f_{7/2}$, 71.30 eV; $4f_{5/2}$, 74.50 eV) and bulk Pd ($3d_{5/2}$, 335.20 eV; $3d_{3/2}$, 341.10 eV), suggesting the electronic interactions between PdPt and GDY [43]. Together, these results reveal that the PdPt nanoparticles are electronically coupled with GDY, rather than being physically deposited without interactions. According to our previous theoretical calculations, we hypothesized that disordered PdPt nanoparticles are anchored at the carbon-carbon triple bonds of GDY [28]. Furthermore, the peaks of PdPt/GDY match well with those in the corresponding simulated XRD pattern of PdPt alloy, supporting the formation of the PdPt alloy phase (Fig. S3b).

2.2 Operando luminol ECL evaluation of ROS production.

ROS electrosynthesis could be generally performed during ORR and HPRR through two routes: (1) HPRR proceeding through $\text{H}_2\text{O}_2 \rightarrow \cdot\text{OH}$ followed by $\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{O}_2^{\cdot-} + \text{H}_2\text{O}$, and (2) ORR yielding various ROS ($\cdot\text{OH}$, $\text{O}_2^{\cdot-}$) directly from O_2 , according to the previous reports [25, 44]. The reaction of the produced ROS and luminol (LH-) would generate the excited state luminol (AP_2^{2-*}) and produce luminescence, enabling operando ROS monitoring with high sensitivity, where ECL intensity directly corresponds to the amount of ROS, as scheme illustrated in Fig. 2a. To operando evaluate the produced ROS during ORR and HPRR, we firstly evaluated the electrocatalytic performance of the PdPt/GDY toward ORR and HPRR with cyclic voltammetry (CV) in phosphate buffer at pH 7.4. In Fig. 2b, CVs obtained at the

PdPt/GDY-modified GCE (PdPt/GDY/GCE) exhibited a reduction peak (peak current, $2.25\ \mu\text{A}$) at a potential of -0.20 V (vs. Ag/AgCl) in ambient air-saturated phosphate buffer. The peak was not recorded in N_2 -saturated phosphate buffer, confirming its origin from ORR. We then added $400\ \mu\text{M}\ \text{H}_2\text{O}_2$ into the ambient air-saturated phosphate buffer, and observed an obvious increase (ca. $2.09\ \mu\text{A}$) in the reduction current at the PdPt/GDY/GCE with a peak potential of -0.16 V (vs. Ag/AgCl). Compared with the electrochemical performance of ORR and HPRR at bare GCE (Fig. S4), the positively shifted reduction potential at PdPt/GDY (Fig. 2b) indicates that PdPt/GDY can catalyze the reduction of H_2O_2 . Then, we added $100\ \mu\text{M}\ \text{L-012}$ (8-amino-5-chloro-7-phenylpyrido[3,4-d] pyridazine-1,4[2H,3H]-dione) into the ambient air-saturated buffer to detect ROS generated during the process of ORR and HPRR. L-012, luminol derivative, was chosen as the luminophore because of its excellent luminous efficiency [45]. We found that, with the PdPt/GDY as the catalyst, the ECL intensity of L-012 obtained after the addition of H_2O_2 was almost 29 times higher than that observed in ambient air-saturated phosphate buffer (Fig. 2c), suggesting that the amount of ROS synthesized through HPRR is higher than that through ORR with the PdPt/GDY electrocatalyst. Notably, although HPRR and ORR exhibited similar reduction currents, their ECL responses were markedly different. This divergence underscores the unique advantage of operando ECL, which reveals differences in radical production that cannot be discerned from the current intensities alone.

To demonstrate the highly efficient electrosynthesis of ROS with the PdPt/GDY catalyst, we investigated and compared the ECL performance during ORR and HPRR with different nanomaterials including pristine GDY, single metal-supported GDY (i.e., Pd/GDY and Pt/GDY), physically mixed $\text{Pd}/\text{GDY} + \text{Pt}/\text{GDY}$, bimetallic PdPt-supported onto GDY with different Pd-to-Pt ratios, and PdPt-supported onto other carbon substrate. These materials were confined onto GCEs for electrochemical and ECL studies. As shown in Fig. S5, pristine GDY, Pd/GDY , Pt/GDY , and physically mixed $\text{Pd}/\text{GDY} + \text{Pt}/\text{GDY}$ exhibit no evident ECL signal during either ORR or HPRR, indicating that less ROS is produced with these materials compared with the PdPt/GDY catalyst. In addition, we synthesized the PdPt/GDY with various Pd-to-Pt ratios to study the effect of Pd:Pt ratio on the efficiency of the electrosynthesis of ROS. The ratio of nominal concentrations of Pd and Pt used during the synthesis (abbreviated as $\text{Pd}_3\text{Pt}/\text{GDY}$, PdPt/GDY and $\text{Pd}_2\text{Pt}/\text{GDY}$) closely corresponded to the relative elemental compositions measured with inductively coupled plasma-mass spectrometry (ICP-MS) (Table S1). The ECL signal progressively decreased at the 3:1 ($\text{Pd}_3\text{Pt}/\text{GDY}$) and 2:1 ($\text{Pd}_2\text{Pt}/\text{GDY}$) ratios, with the ECL intensity of PdPt/GDY being 2.1-fold and 8.1-fold higher than those of $\text{Pd}_2\text{Pt}/\text{GDY}$ and $\text{Pd}_3\text{Pt}/\text{GDY}$, respectively (Fig. 2d), indicating that the maximum amount of ROS could be produced with the PdPt/GDY as the catalyst, likely due to the enhanced Pd-Pt alloying at the 1:1 composition, which optimizes the electronic structure for ROS electrosynthesis [46].

To demonstrate the effect of substrate materials on the performance of ROS electrosynthesis, electroless deposition

of PdPt was performed onto other carbon substrates including multi-walled carbon nanotubes (MCNTs), graphene (GR), and graphene oxide (GO) with the same procedures as those used for the deposition of PdPt onto GDY. HRTEM images of different carbon-based PdPt composites show the confinement of metal nanoparticles on the surface of the carbon substrate with uniform elemental distribution of C, Pd and Pt, indicating that Pd and Pt were successfully deposited onto the carbon substrate (Fig. S6). The ECL intensity observed at all carbon-supported PdPt during HP RR was higher than that during ORR (Fig. S7), and the ECL enhancement during HP RR at different carbon substrate follows the hierarchy: PdPt/GR < PdPt/MCNT < PdPt/GO < PdPt/GDY (Fig. 2e), with the ECL intensity of PdPt/GDY being 1.7-fold, 2.4-fold, and 5.0-fold higher than those of PdPt/GO, PdPt/MCNT, and PdPt/GR, respectively. Notably, the ECSA of the carbon-supported PdPt catalysts follows the opposite order, with PdPt/GDY < PdPt/GO < PdPt/MCNT < PdPt/GR (Fig. S8), suggesting that the superior ROS electrosynthesis performance of PdPt/GDY may not be ascribed to a larger electrochemically active surface area. These results reveal that GDY-supported PdPt catalyst exhibits the most pronounced activity for electrosynthesis of ROS through HP RR, which may be attributed to the synergistic effect of Pd–Pt alloying and the EMSI between PdPt nanoparticles and GDY. Such dual

regulation is expected to modulate the d-band electronic structure of the active metal sites, thereby optimizing the generation, conversion, and desorption of key oxygen-containing intermediates during HP RR, ultimately promoting efficient ROS generation.

To verify the production of ROS at -0.20 V through HP RR, a constant potential of -0.20 V was applied to the PdPt/GDY-confined GCE in 0.1 mol/L phosphate buffer (pH 7.4) containing 200 μM H_2O_2 for 100 s, then the potential was stopped and 100 μM L-012 was injected into the buffer. As shown in Fig. 3a, no luminescence signal was observed during the constant potential electrolysis, whereas a strong chemiluminescence signal was generated upon the addition of L-012. The signal slowly decayed after stopping the potential polarization, suggesting the electrocatalytic production of ROS from HP RR. Strong ECL emission was observed with the PdPt/GDY catalyst in 0.1 mol/L phosphate buffer (pH 7.4) containing 100 μM L-012 and 200 μM H_2O_2 when the potential applied on the electrode was stepped to -0.30 V, whereas the ECL intensity immediately decreased when the potential was stepped to +0.30 V (Fig. S9a) and even to +0.10 V (Fig. S9b, and S9c), further indicating that ROS is produced through HP RR. This result was further confirmed by the stronger ECL intensity observed with increasing negative potentials (Fig. S9d, S9e and S9f).

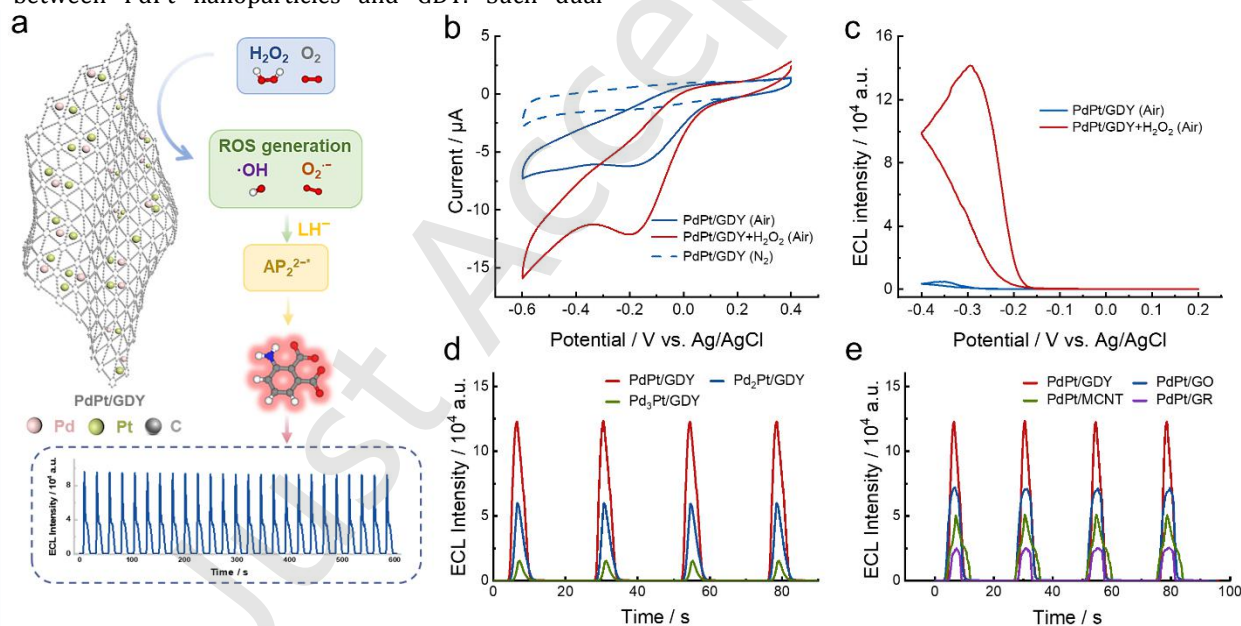


Figure 2. Efficient synthesis and ECL-based operando evaluation of ROS with PdPt/GDY catalyst. (a) Schematic diagram of ECL induced by ROS generated from H_2O_2 or O_2 catalyzed by PdPt/GDY. (b) CVs obtained with the PdPt/GDY-modified GC electrode in 0.1 M phosphate buffer (pH 7.4) saturated with ambient air (solid line) or N_2 (dotted line) in the presence (red) or absence (blue) of 400 μM H_2O_2 . Potential scan rate: 100 mV s^{-1} . (c) ECL intensity-potential curves obtained with the PdPt/GDY-modified GC electrode in 0.1 M phosphate buffer (pH 7.4) containing 100 μM L-012 with (red) or without (blue) 400 μM H_2O_2 . (d) ECL-time curves obtained at the PdPt/GDY/GCE, Pd₂Pt/GDY/GCE, and Pd₃Pt/GDY/GCE in phosphate buffer containing 100 μM L-012 and 400 μM H_2O_2 under a continuous potential scanning from -0.40 to +0.20 V. (e) ECL-time curves obtained at the PdPt/GDY/GCE, PdPt/GO/GCE, PdPt/MCNT/GCE, and PdPt/Gr/GCE in phosphate buffer containing 100 μM L-012 and 400 μM H_2O_2 under a continuous potential scanning from -0.40 to +0.20 V. Potential scan rate: 100 mV s^{-1} .

To clarify the types of ROS electro-synthesized through HP RR with the PdPt/GDY catalyst, two typical ROS

scavengers (thiourea and nitroblue tetrazolium, NBT) were added in the phosphate buffer containing 100 μM L012 and

200 μM H_2O_2 . Thiourea and NBT were used as the radical scavengers to clear $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ [25, 47], respectively. As depicted in Fig. 3b, thiourea induces around 100% quenching rate of ECL signal, while NBT results in less than 60% signal reduction, indicating that $\cdot\text{OH}$ is the primary species of the electro-synthesized ROS.

The stability of ROS synthesis with the PdPt/GDY catalyst was assessed in phosphate buffer with 100 μM L-012 and 200 μM H_2O_2 . As shown in Fig. 3c, the PdPt/GDY catalyst exhibits exceptional ECL stability, retaining stable for 25 cycles tests with a relative standard deviation of 2.1%. To evaluate the long-term stability of the PdPt/GDY catalyst, we monitored the ECL intensity during continuous operation for 11 h as an indicator of the content of ROS. The ECL signal remained essentially unchanged throughout the prolonged electrolysis (Fig. S10), suggesting that the ROS electrosynthesis capability of PdPt/GDY was well maintained during long-term operation. Furthermore, post-reaction characterization was performed to investigate the structural and chemical stability of the catalyst. HRTEM

images of PdPt/GDY after 11 h electrolysis reveal that PdPt nanoparticles remain uniformly dispersed on the GDY support (Fig. S11a). The average nanoparticle size after electrolysis is approximately 2.2 nm (Fig. S11b), which is almost unchanged compared with the fresh catalyst (2.1 nm), indicating the structural stability of PdPt nanoparticles during prolonged operation. The XPS spectra of PdPt/GDY after 11 h electrolysis shows that the binding energy positions of Pd 3d and Pt 4f remain almost unchanged compared with those of the fresh catalyst (Fig. S11c,d). Furthermore, ICP-MS analysis of the electrolyte after 11 h electrolysis reveals only trace amounts of dissolved Pd and Pt species (1.74 and 6.13 $\mu\text{g L}^{-1}$, respectively), confirming the negligible metal dissolution during electrolysis. The above results demonstrate the structural and chemical stability of the PdPt/GDY catalyst during long-term ROS electrosynthesis. This result highlights the high operational stability for electrosynthesis of ROS, attributing to synergistic effect of GDY substrate and PdPt nanoparticles.

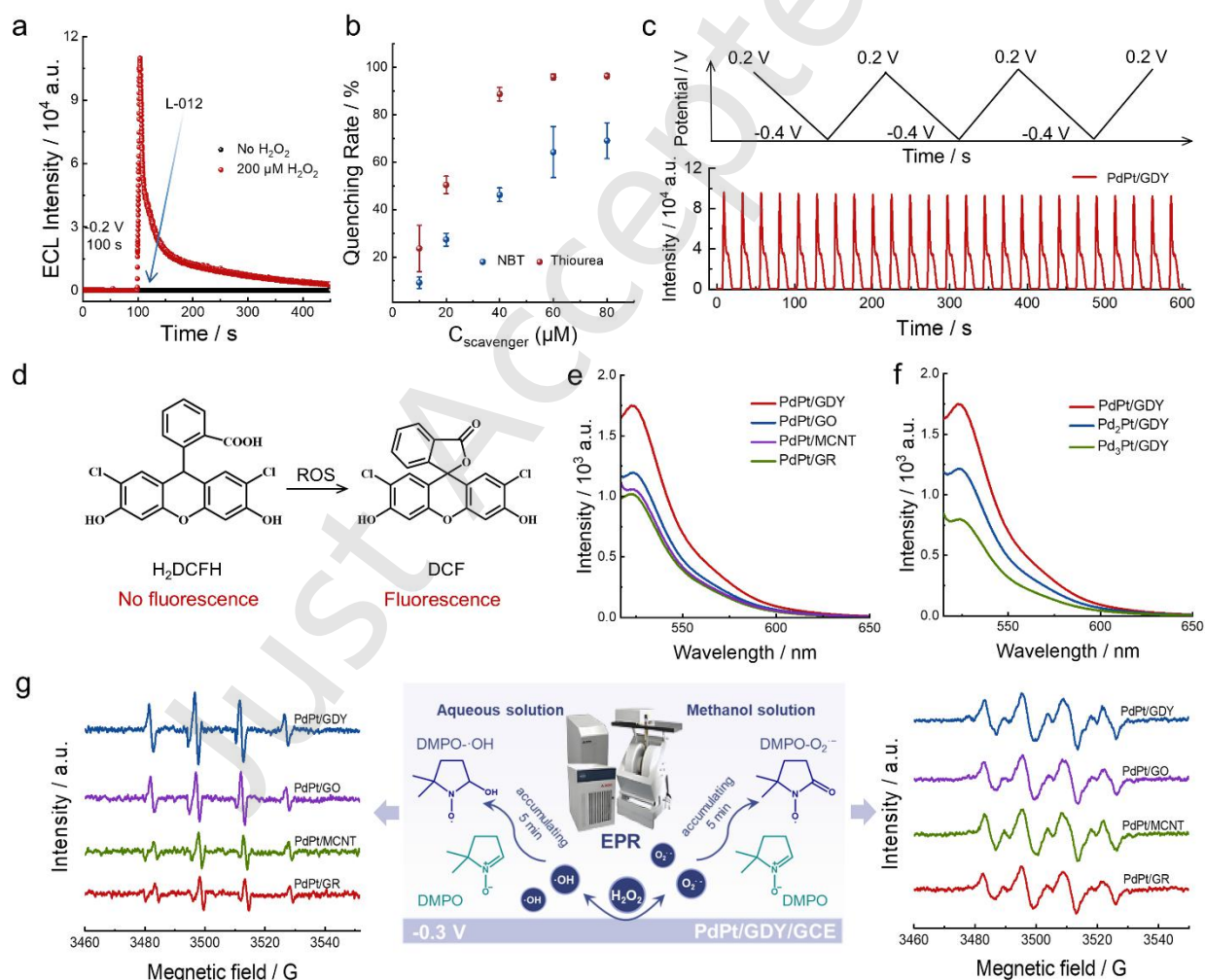


Figure 3. Efficient synthesis and ex situ evaluation of ROS with PdPt/GDY catalyst. (a) ECL intensity obtained at the PdPt/GDY-modified GC electrode in 0.1 M phosphate buffer containing 200 μM H_2O_2 (pH 7.4) at -0.20 V for 100 s, followed by the addition of 100 μM L-012 as labelled in the Figure. (b) Quenching rate of ECL intensity after the addition of radical scavenger into 0.1 M phosphate buffer containing 100 μM L-012 and 200 μM H_2O_2 (pH 7.4). Thiourea and NBT were used as radical scavengers to clear $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$, respectively. (c) ECL-time curves obtained at the PdPt/GDY-modified GC electrode in phosphate buffer containing 100 μM L-012 and 200 μM H_2O_2 under a continuous potential scanning from -0.40 to +0.20 V for

25 cycles. (d) Schematic diagram of ROS monitoring with DCDHF and fluorescence spectra of DCDHF obtained with PdPt/GDY-, PdPt/GO-, PdPt/GR-, PdPt/MCNT-modified GC electrodes (e) as well as PdPt/GDY-, Pd₂Pt/GDY-, Pd₃Pt/GDY-modified GC electrodes (f) in 0.1 M phosphate buffer containing 200 μ M H₂O₂. The electrodes were poised at -0.20 V for 40 min. (g) Schematic diagram of EPR detection for different types of radicals (middle). EPR spectra of PdPt/GDY-, PdPt/GO-, PdPt /GR-, and PdPt /MCNT-modified GC electrodes in 0.1 M phosphate buffer (pH 7.4) containing 200 μ M H₂O₂ and DMPO in aqueous solution (left) or in methanol solution (right), the electrode was poised at -0.30 V for 5 min.

We also investigated the sources, quantities, and types of ROS electro-synthesized with disparate carbon-based PdPt nanocomposites and PdPt/GDY with various Pd-Pt ratios as the catalysts. Given that most metal nanomaterials have enzyme mimicking properties and ROS will be generated during catalysis [48-49], we investigated whether the enzyme-like properties of disparate carbon-based Pd-Pt nanocomposites contribute to the electrosynthesis of ROS. As shown in Fig. S12, the PdPt composite nanomaterials exhibited no chemiluminescence signals in the solution containing L-012 and H₂O₂, ruling out the contribution of enzyme mimetic properties of PdPt/GDY to the electrosynthesis of ROS. Typical fluorescent probe, 2',7'-dichlorodihydrofluorescein (DCDHF) [26, 50-51], was used for monitoring the amount of ROS generated during HP RR in terms of the green fluorescent dichlorofluorescein (DCF) produced by the reaction of DCDHF with ROS (Fig. 3d). We

added DCDHF into phosphate buffer containing 200 μ M H₂O₂ and measured the fluorescent intensity after poisoning the working electrode modified with different electrocatalysts at a potential of -0.20 V for 40 min (Fig. 3e and Fig. S13). Within 40 min, the buffer with the PdPt/GDY as electrocatalyst exhibits the strongest luminescence among PdPt composite nanomaterials with different Pd-Pt ratios confined onto GDY (Fig. 3f), with the fluorescence intensity of PdPt/GDY being 1.5-fold, 1.6-fold, 1.7-fold, 1.4-fold and 2.1-fold higher than those of PdPt/GO, PdPt/MCNT, PdPt/GR, Pd₂Pt/GDY and Pd₃Pt/GDY, respectively. These results indicate that the PdPt/GDY produces the highest amount of ROS compared to other PdPt-containing catalysts. The high efficiency in synthesizing ROS with the PdPt/GDY was consistent with our operando ECL results. Notably, operando ECL features high sensitivity, enabling monitoring the synthesized ROS with high time resolution.

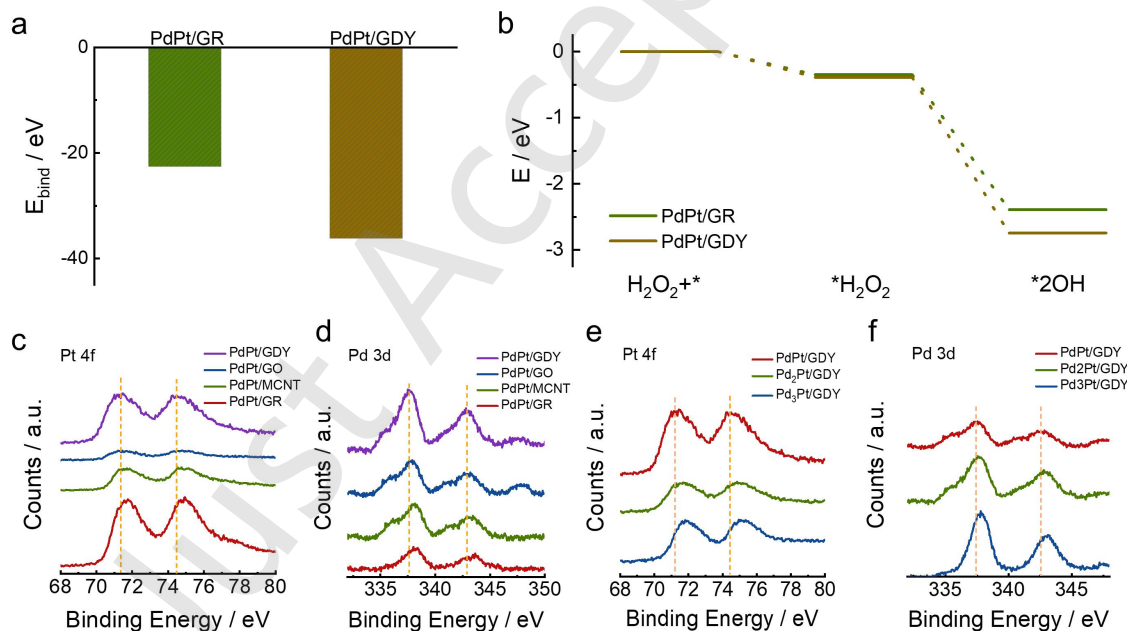


Figure. 4. Mechanism for efficient ROS electrosynthesis with the PdPt/GDY catalyst. (a) Binding energy analysis of PdPt nanoparticles supported by graphdiyne and graphene. (b) Free energy barriers of the H₂O₂ reduction on PdPt/GDY and PdPt/GR. (c) Pt 4f and (d) Pd 3d XPS spectra of PdPt/GDY, PdPt/GO, PdPt/MCNT, and PdPt/GR. (e) Pt 4f and (f) Pd 3d XPS spectra of PdPt/GDY, Pd₂Pt/GDY, and Pd₃Pt/GDY.

We further investigated the efficiency of electrosynthesis of ROS and ROS speciation through HP RR catalyzed by carbon-supported PdPt nanocomposites with ex situ electron paramagnetic resonance (EPR) technique using 5,5-dimethyl-1-pyrrolidine N oxide (DMPO) as a spin trap to form DMPO adducts with ROS. Because, in aqueous solution, DMPO combines selectively with $\cdot$ OH to form stable adducts (DMPO- $\cdot$ OH). While, in methanol solution, DMPO combines with O₂⁻ to form DMPO- O₂⁻ because methanol can

scavenge $\cdot$ OH, as reported previously [25]. As shown in Fig. 3g, DMPO captures produced $\cdot$ OH and O₂⁻ in aqueous and methanol solutions, respectively, forming DMPO- $\cdot$ OH and DMPO- O₂⁻ adducts (both accumulated for 5 min) with characteristic signals obtained by EPR. The intensity of the DMPO- $\cdot$ OH signal was the strongest for PdPt/GDY as electrocatalyst and the weakest for PdPt/GR, which was consistent with our operando ECL results. Notably, all four composites demonstrated detectable yet minimally

differentiated $O_2^{\cdot-}$ signals, showing that $\cdot OH$ constitutes the predominant ROS generated through the HPRR with the PdPt/GDY catalyst. Next, we compared the efficiency of ROS electrosynthesis through ORR and HPRR using the PdPt/GDY as electrocatalyst with ex situ EPR and fluorescent

techniques. EPR analysis (Fig. S14) demonstrated that the DMPO- $O_2^{\cdot-}$ signal during ORR was much smaller than that during HPRR, while the DMPO- $\cdot OH$ adduct signal was negligible during ORR, indicating that ROS were predominantly generated through HPRR rather than ORR.

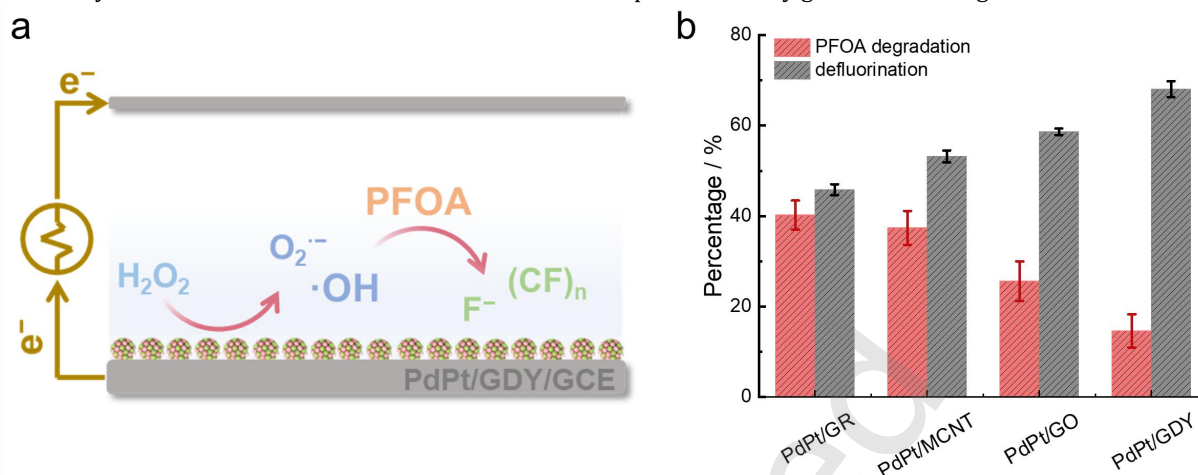


Figure 5. Application in PFOA degradation. (a) Schematic diagram of PdPt/GDY electrocatalytic H_2O_2 generating ROS to degrade PFOA. (b) PFOA degradation rate and (d) defluorination of PdPt/GDY, PdPt/GO, PdPt/MCMT, and PdPt/GR on PFOA in 0.5 M Na_2SO_4 containing 200 μM H_2O_2 . The electrodes were poised at -0.30 V for 200 min.

2.3 Mechanism for efficient synthesis of ROS by PdPt/GDY.

To investigate the intrinsic mechanism by which GDY modulates ROS electrosynthesis with PdPt catalyst through HPRR, we conducted density functional theory (DFT) calculations. The binding energy analysis (Fig. 4a) reveals that GDY exhibits stronger metal-substrate interactions with PdPt nanoparticles (-36.19 eV) compared to GR (-22.55 eV), demonstrating the superior stabilization capability of GDY for metal loading systems. More importantly, the thermodynamics of H_2O_2 activation on PdPt/GDY and PdPt/GR were compared (Fig. 4b) to elucidate the effect of the carbon substrate on the HPRR pathway. Specifically, H_2O_2 adsorption and the subsequent O-O bond cleavage are thermodynamically favorable on both PdPt/GDY and PdPt/GR. The calculated H_2O_2 adsorption energies are -0.39 and -0.35 eV, respectively, indicating slightly more favorable adsorption on PdPt/GDY. After adsorption, the overall energy changes during O-O bond cleavage are -2.74 and -2.39 eV for PdPt/GDY and PdPt/GR, respectively. Thus, O-O bond cleavage is thermodynamically downhill on both catalysts, while PdPt/GDY provides a 0.35 eV larger thermodynamic driving force for this step. These results suggest that, compared with GR, the GDY substrate promotes H_2O_2 activation by slightly strengthening H_2O_2 adsorption and providing a greater thermodynamic driving force for O-O bond cleavage, which may favor the generation of ROS radicals during HPRR. Note that these results represent thermodynamic trends obtained from the corrected slab models, rather than electrochemical activation barriers under a specific potential or solvent environment. Charge density difference analysis (Fig. S15) reveals distinct interfacial interactions, the positively charged GR surface withdraws electrons from adsorbed $\cdot OH$ (0.825 e), enhancing the O-catalyst bonding and increasing the binding energy, which impedes $\cdot OH$ desorption [52]. Conversely, the

electron-rich GDY surface donates electrons to $\cdot OH$ (0.684 e), weakening its O-H bond and reducing the binding energy, thereby facilitating $\cdot OH$ desorption [53]. Consequently, the H_2O_2 reduction exhibits more favorable thermodynamics on the PdPt/GDY, which originates from the unique electron exchange between GDY and metals.

The high efficiency of ROS electrosynthesis with the PdPt/GDY may originate from the synergistic electronic interaction among Pd, Pt, and GDY. The high efficiency of ROS electrosynthesis with the PdPt/GDY may be attributed to the synergistic effect of Pd-Pt alloying and the interaction between PdPt and GDY, as supported by XPS analysis (Fig. 4c-4f). The Pt 4f and Pd 3d binding energies of PdPt/GDY exhibit clear negative shifts compared with those of other PdPt-containing catalysts, indicating charge redistribution among Pd, Pt, and GDY. Such a change in the electronic environment may influence the d-band of the active metal sites, thereby optimizing the adsorption of oxygen-containing intermediates during HPRR. Combined with the DFT results showing a lower energy barrier for $\cdot OH$ generation on PdPt/GDY, these findings suggest that the optimized electronic structure favors ROS formation kinetics, leading to the highly efficient ROS electrosynthesis observed on PdPt/GDY.

2.4 Application in PFOA degradation.

Per- and polyfluoroalkyl substances (PFAS), particularly PFOA, are persistent contaminants that pose serious environmental and human health risks because of their exceptional chemical stability and resistance to natural degradation [54-58]. Electrochemical advanced oxidation processes are promising for PFOA degradation because they can generate ROS such as $\cdot OH$ and $O_2^{\cdot-}$ that serve as powerful oxidants for C-F bond cleavage [59-60]. To demonstrate the practical utility of our ROS electro-synthetic system with PdPt/GDY catalyst, we first employed tetracycline (TC), a representative antibiotic contaminant, as a model substrate

to study the ROS-driven degradation. TC exhibits characteristic absorption peaks at 270 and 360 nm. After 100 min treatment with electro-synthesized ROS, the intensity of absorption peak decreases greatly, showing the efficient degradation. TC removal rate reaches $83 \pm 5\%$ within 100 min, which is higher than those with PdPt/GO, PdPt/MCNT, and PdPt/GR ($55 \pm 2\%$, $48 \pm 3\%$ and $27 \pm 4\%$, respectively, Fig. S16) as the electrocatalysts. These results demonstrate the high capability of the PdPt/GDY-based ROS electro-synthetic system for rapid TC degradation through boosting the ROS production.

Encouraged by these results, we then evaluated PFOA degradation with ROS electro-synthetic system based on different carbon-supported PdPt catalysts (Fig. 5a). As shown in Fig. S17, Fig. S18 and Fig. 5b, PdPt/GDY, PdPt/GO, PdPt/MCNT, and PdPt/GR achieve PFOA degradation efficiencies of 85.4%, 74.4%, 62.6%, 59.8%, respectively. Given that the apparent loss of PFOA may primarily reflect transformation into fluorinated intermediates, we therefore evaluated the defluorination capability of these four catalysts. PdPt/GDY exhibits the highest defluorination efficiency (68.1%) compared to PdPt/GO (58.7%), PdPt/MCNT (53.2%), and PdPt/GR (45.8%). Notably, the defluorination efficiency gradually reaches a plateau as the reaction time is prolonged. To determine whether this plateau is associated with H_2O_2 depletion, the residual H_2O_2 concentration was monitored throughout the reaction (Fig. S19). The H_2O_2 concentration continuously decreased without reaching a plateau, with less than 20% of the initial H_2O_2 consumed after 200 min for PdPt/GDY. These results indicate that H_2O_2 remains available throughout the reaction and is unlikely to be the limiting factor for defluorination. The observed defluorination plateau is therefore more likely associated with the relatively slower cleavage of C-F bonds in PFOA-derived fluorinated intermediates. [58, 60-61] Collectively, these results indicate that the GDY-supported PdPt nanocomposite markedly promotes ROS generation during the HPRR process, thereby accelerating deep defluorination and degradation of PFOA.

CONCLUSIONS

In summary, we developed PdPt/GDY as efficient electrocatalysts for ROS synthesis and established luminol ECL as an operando probe of ROS. The operando ECL analysis reveals that the PdPt/GDY achieves markedly higher ROS synthesis than PdPt on conventional carbon supports as well as PdPt/GDY with various Pd-Pt ratios. Mechanistic studies attribute the enhanced activity to the synergistic effects between Pd and Pt and between PdPt and GDY. The enhanced ROS electrosynthesis of PdPt/GDY enables superior PFOA degradation and defluorination among all carbon-supported PdPt analogues, highlighting its high capability for the deep degradation of persistent fluorinated pollutants. We anticipate that this work will extend beyond PdPt/GDY to guide the rational design of ROS electrocatalysts and provide a framework for environmental and biomedical applications.

Electronic Supplementary Material: Supplementary material (chemicals and reagents; apparatus and

measurements; reduction potential of Pd/GDY; fluorescence and working function measurements; contaminants degradation and chemiluminescence measurements; DFT calculations; morphological characterization, size distribution, XPS, CVs, ECL- potential curves, HRTEM images of PdPt/GO, PdPt/GR and PdPt/MCNT, ECL- time curves, enzyme- like properties, ROS distribution, fluorescence intensity and EPR spectra, binding energy and free- energy diagrams, charge density differences, UV- vis absorption spectra, and ICP- MS data) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909196>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request

Acknowledgements

We greatly acknowledge the financial support from the National Basic Research Program of China (2024YFA1803400, 2024YFA1803403, 2022YFA1204500 and 2022YFA1204503) and the National Natural Science Foundation of China (Grant Nos. 22174162, 22134002 and 22425405)

Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

M. Z. and L. M. designed the research. G. R., N. G., S. Z., R. L. designed, fabricated and analyzed devices. Y. W., H. C. and G. R. designed and performed the DFT calculations. M. Z., L. M., Y. W., Z. S. and G. R. wrote the manuscript.

Use of AI statement

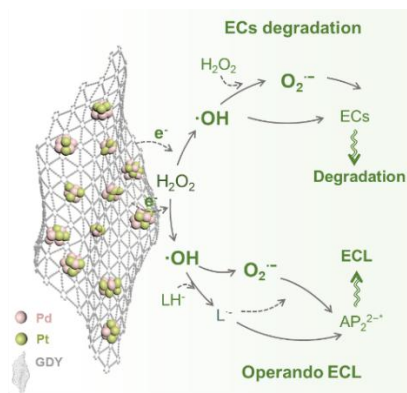
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Graphdiyne-supported PdPt catalyst boosts the electrosynthesis of reactive oxygen species

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Supporting information to <https://doi.org/10.26599/NR.2026.94909196>

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1. Supplementary methods

Chemicals and reagents

All reagents including H_2O_2 , K_2PdCl_4 , K_2PtCl_4 , and NaBH_4 were sourced from Sinopharm Chemical Reagent Co., Ltd. 2',7'-Dichlorofluorescein diacetate (DCFH-DA) and 8-amino-5-chloro-7-phenylpyrido[3,4-d] pyridazine-1,4[2H,3H]-dione (L-012) were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Thiourea, nitro blue tetrazolium (NBT), hydrochloric acid (HCl) and ethanol were bought from Sinopharm Chemical Reagent Co., Ltd. 5,5-dimethyl-1-pyrrolidine N oxide (DMPO) was purchased from Sigma Aldrich. All these chemicals were used without purifications and all the solutions were prepared using milli-Q water.

Apparatus and measurements

All electrochemical and electrochemiluminescent (ECL) experiments were conducted in a standard three-electrode cell by use of a computer-controlled Autolab electrochemical analyzer. Glassy carbon (GC) electrode was used as working electrode and a platinum wire and Ag/AgCl (filled with saturated KCl) were used as counter electrode and reference electrode, respectively. The ECL signals were simultaneously measured along with CV curves using BPCL ultra-weak luminescence analyzer. The photomultiplier tube (PMT) was biased at 900 V. All electrochemical experiments were performed at room temperature. Fluorescent spectra were recorded on a Hitachi F-4600 luminescence spectrometer. Scanning electron microscopy (SEM) was carried out with a Hitachi SU8010 scanning electron microscope. High-resolution transmission electron microscopy (HRTEM), and elemental mapping were carried out on a Talos F200s (Thermo Fisher, United States). Raman spectra were conducted on Xplora plus. UV-vis absorbance spectra were recorded using Cary 60 spectrophotometer. Electron paramagnetic resonance (EPR) spectra were conducted on E-500 (Bruker German). Inductively coupled plasma-mass spectrometry (ICP-MS) was conducted on NexION 300D (Perkin Elmer, United States). Ultraviolet photoelectron spectra (UPS) were conducted on Escalab 250Xi (Thermo Fisher, United States).

Preparation of PdPt/GDY

GDY powder was dispersed in deionized water obtaining a GDY dispersion of 0.5 mg/mL. 0.2 mL of K_2PdCl_4 aqueous solution (10 mM) was added to 2 mL of the GDY dispersion (0.5 mg/mL) and stirred in an ice bath for 30 minutes. Centrifuging and washing the product with water removed unreacted substances, resulting in the Pd/GDY. Then, 0.1 mL of K_2PtCl_4 (10 mM) was added to 1 mL of the Pd/GDY dispersion (0.5 mg/mL) and stirred in an ice bath for 30 min. The product was centrifuged and washed with water to remove unreacted species. After that, 0.5 mL of NaBH_4 (10 mM) was added and stirred for another 30 min. Centrifuging and washing the product with water removed unreacted substances, resulting in the PdPt/GDY. The preparation procedure for PdPt/GR, PdPt/GO, and PdPt/MCNT is similar to that of PdPt/GDY. Replacing GDY with GR, GO, and MCNT respectively, and the other operating steps were the same.

The reduction potential of Pd/GDY

The reduction potential of Pd/GDY was calculated through the follow equations:

$$\phi = h\nu - E_{\text{Fermi}} + E_{\text{cutoff}}$$

$$\phi/e = E(\text{vs SHE}) + 4.44 \text{ V}$$

where $h\nu$, E_{Fermi} , and E_{cutoff} are 21.22 eV, 21.08 eV and 4.22 eV, respectively. $E(\text{vs. SHE})$ was calculated to be -0.08 V.

Fluorescence measurements

The fluorescence measurement method for DCFH-DA reaction with ROS generated under different time was as follows: A constant potential of -0.20 V was applied to PdPt/GDY-, PdPt/GO-, PdPt/GR-, PdPt/MCNT, Pd₂Pt/GDY- and Pd₃Pt/GDY-confined GCE in 0.1 mol/L phosphate buffer (pH 7.4) containing 200 μM H_2O_2 and 5 μM DCFH-DA for different time. The fluorescence spectra of the solution were recorded in real-time using an F-4600 fluorescence spectrometer (Hitachi, Japan).

The measurement of Pd/GDY working function

To explore the direct redox reaction property of the Pd/GDY with PtCl_4^{2-} ion, E_{cutoff} values of Pd/GDY was measured with UPS. The

work functions (Φ) were thus calculated via the following equation: ^{1,2}

$$\phi = h\nu - E_{Fermi} + E_{cutoff}$$

where $h\nu$, E_{Fermi} , and E_{cutoff} are the photo energy of the excitation light (21.22 eV), the Fermi level edge (21.08 eV in this case), and the inelastic secondary electron cutoff measured in Figure S 1. The reduction potential was obtained from the equation as follow: ³⁻⁵

$$\phi/e = E(vs SHE) + 4.44 V$$

where Φ is the work functions, E is the reduction potential versus standard hydrogen electrode (SHE).

Contaminants degradation by electrosynthesis ROS

TC degradation: A constant potential of -0.30 V was applied to the PdPt/GDY-confined carbon paper in 0.1 mol/L phosphate buffer (pH 7.4) containing 200 μ M H_2O_2 and 50 μ M TC for 100 min, subsequently detected by UV spectrophotometer. The standard three electrode system was used for electrochemical degradation. Carbon paper was chosen as the working electrode with an effective working area of 1 cm² and was modified with 1 mg/mL PdPt/GDY. Pt wire and Ag/AgCl (saturated KCl) were used as the counter electrode and reference electrode, respectively.

The removal ratio of TC (η , %) was calculated via the following equation:

$$\eta = \frac{A_0 - A_t}{A_0} \times 100\%$$

where A_0 and A_t were the absorbance of target contaminants at the starting time and specific reaction time (t), respectively.

PFOA degradation. A series of PFOA standard solutions with concentrations of 0.5, 1, 2, 5, 10, 15, and 20 mg L⁻¹ were prepared in 0.5 M Na_2SO_4 , and the calibration curve of PFOA was obtained by HPLC for quantification of unknown samples. In a solution containing 200 μ M H_2O_2 and 20 mg L⁻¹ PFOA (pH 7.4), carbon paper loaded with PdPt/GDY was subjected to a constant potential of -0.30 V for 200 min. During electrolysis, 1 mL aliquots were withdrawn from the degradation reactor every 50 min using a syringe and immediately filtered through a 0.22 μ m syringe membrane for determination of PFOA consumption by HPLC and fluoride concentration by a fluoride ion-selective electrode. Carbon paper with an effective working area of 4 cm² was used as the working electrode and modified with 1 mg mL⁻¹ PdPt/GDY. A Pt wire and Ag/AgCl (saturated KCl) electrode were used as the counter and reference electrodes, respectively. All degradation experiments were performed three times under identical conditions. The concentration of PFOA was determined by HPLC-UV using a Zorbax Eclipse Plus C18 column (4.6 mm $\times$ 250 mm $\times$ 5 μ m). The mobile phase consisted of acetonitrile and ultrapure water (60:40, V:V), and the UV detection wavelength was set at 210 nm. The production of F^- was determined by a fluoride ion-selective electrode. The preparation of total ionic strength adjustment buffer (TISAB) was as follows: 85.0 g $NaNO_3$ and 58.5 g $Na_3C_6H_5O_7 \cdot 2H_2O$ were dissolved in water and diluted to 1000 mL. Then the pH of the mixed solution was adjusted to 5.5 with HCl. For the measurement of F^- concentration, 1 mL of sample was mixed with 5 mL TISAB and then diluted to 25 mL with deionized water in a volumetric flask. Then, one fluoride ISA powder pillow was added with stirring, and the F^- concentration was measured using a fluoride ion-selective electrode (DX219-F, Mettler Toledo).

Chemiluminescence measurements

To investigate whether the enzyme-like properties of disparate carbon-based PdPt nanocomposites contribute to the electrosynthesis of ROS, 0.1 M phosphate buffer (pH 7.4) containing 200 μ M H_2O_2 and 100 μ M L-012 was mixed with 20 μ L of disparate carbon-based PdPt nanocomposites (0.5 mg/mL) for 5 min, then monitored by an ultra-weak luminescence analyzer (BPCL, Guangzhou).

Density functional theory

Density functional theory (DFT), as implemented in the Vienna Ab initio Simulation Package (VASP), was used for all calculations. ^{6,7} The interaction between ion cores and valence electrons was modeled using the projector augmented wave (PAW) method.⁸

Applying the Perdew-Burke-Ernzerhof (PBE) functional in the generalized gradient approximation (GGA), exchange-correlation effects were addressed.⁹ To ensure computational accuracy, a plane-wave basis set with a 400 eV energy cutoff was employed. A Γ -centered $2 \times 2 \times 1$ k-mesh was employed for Brillouin zone integration, with DFT-D3 dispersion corrections applied to capture long-range interactions.¹⁰ The convergence thresholds were defined as 1×10^{-5} eV for electronic total energy (EDIFF = 1×10^{-5}) and 0.01 eV/Å for ionic forces (contrasting with INCAR's EDIFFG = -0.02 eV/Å). Spin-polarized calculations were performed for all systems to properly account for the unpaired-electron character of the $\cdot\text{OH}$ radical and any associated magnetic effects.

Charge redistribution was investigated through Bader charge analysis using the method developed by Henkelman et al.¹¹ Additionally, charge transfer between system components was visualized through charge density difference analysis implemented in the VASPKIT package.¹²

The two models were constructed using Materials Studio (MS). The graphdiyne system (72 C atoms) was simulated in a hexagonal box with basal plane lattice parameters of 18.91 Å and height 26.00 Å, while the graphene system (72 C atoms) utilized a hexagonal box with basal plane lattice parameters of 14.76 Å and height 20.40 Å. Both systems contained bimetallic nanoclusters comprising 21 Pd and 21 Pt atoms.

The combine energy (E_{com}) was calculated using the equation:

$$E_{\text{com}} = E_{\text{total}} - E_A - E_B$$

where E_{com} represents the interaction energy of the system, E_{total} is the total energy of the combined system, and E_A and E_B are the energies of individual components A and B, respectively.

The charge density difference ($\Delta\rho$) was evaluated using the equation:

$$\Delta\rho = \rho_{AB} - \rho_A - \rho_B$$

where ρ_{AB} represents the charge density of the combined system, and ρ_A and ρ_B are the charge densities of segments A and B, respectively.

We investigated the decomposition mechanisms of hydrogen peroxide on metal clusters supported on graphene and graphdiyne, as well as oxygen decomposition under both acidic and alkaline conditions on these same systems. Based on VASP calculations involving geometry optimizations of key intermediates and transition states along the reaction pathways, we constructed respective energy ladder diagrams for each system.

1. plementary figures and tables

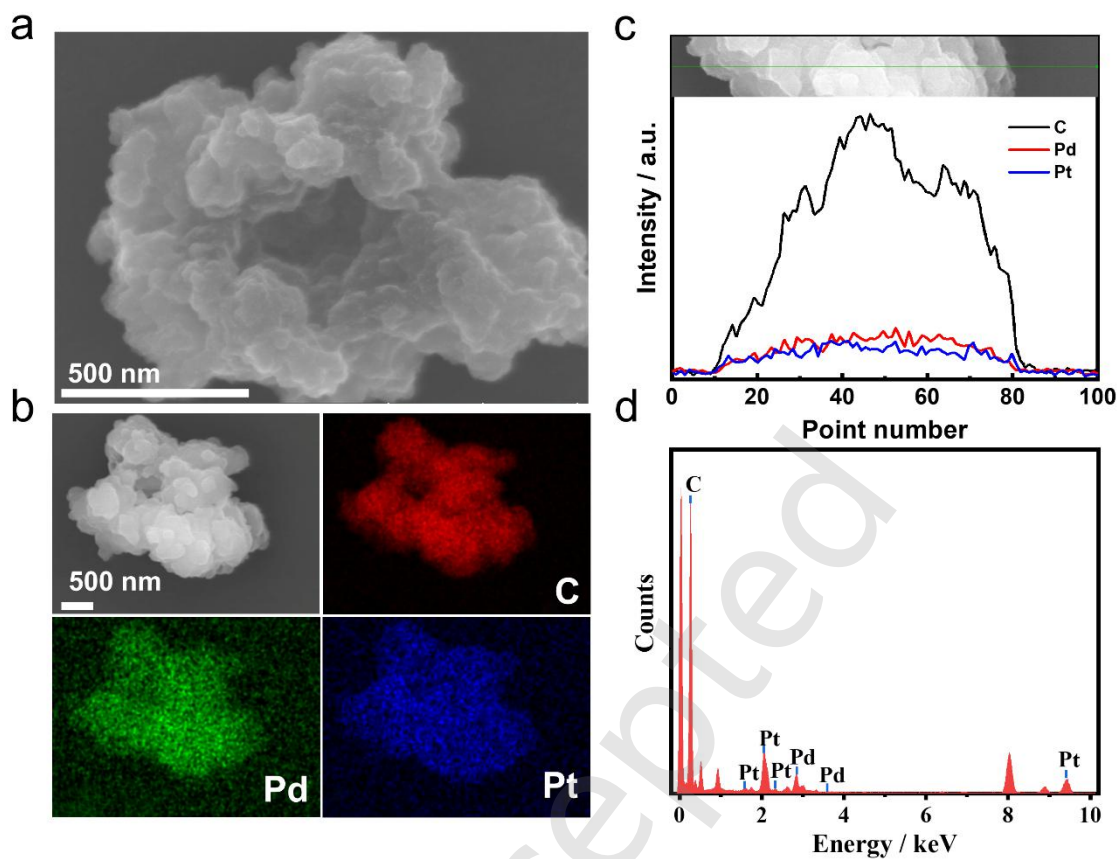


Figure S1. (a) SEM image of PdPt/GDY and (b) the corresponding mapping of C (red), Pd (green) and Pt (blue) of PdPt/GDY. (c) EDS line scanning distribution of PdPt/GDY and (d) EDS spectrum.

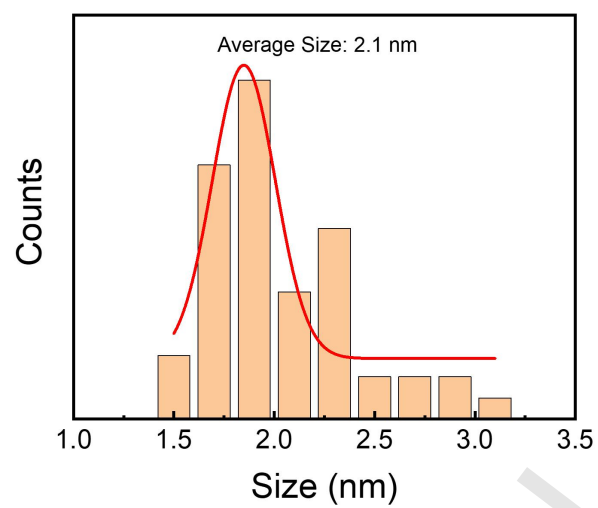


Figure S2. Size distribution of PdPt nanoparticles loaded on GDY.

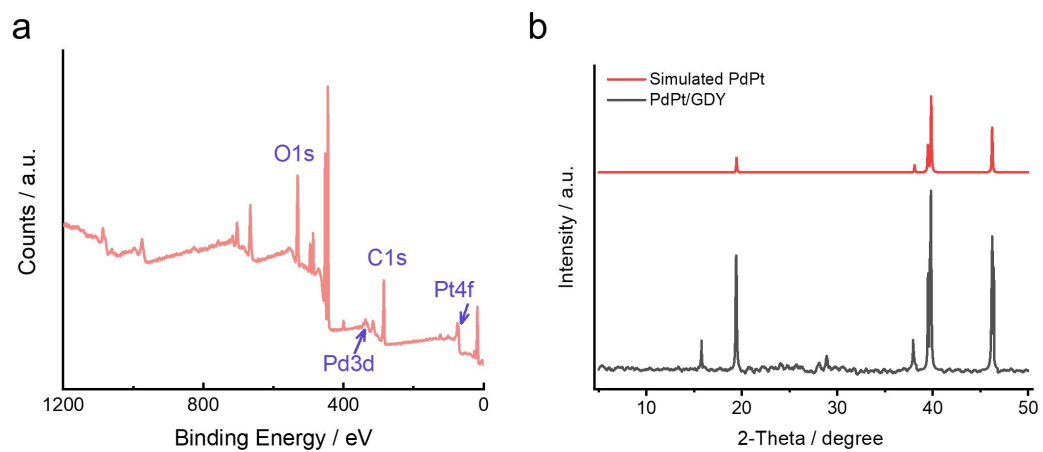


Figure S3. (a) XPS and (b) XRD spectrum of PdPt/GDY.

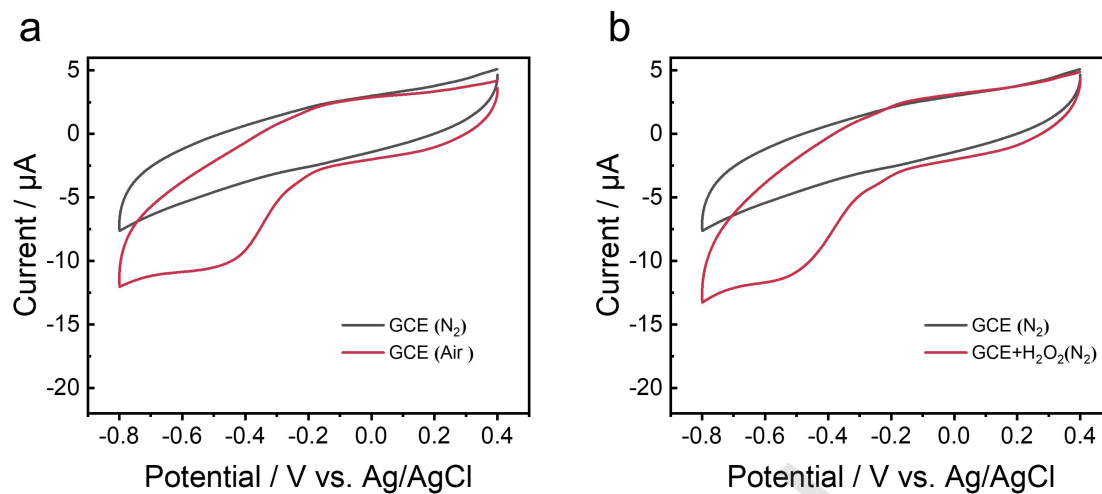


Figure S4. CVs obtained with the GCE in 0.1 M phosphate buffer (pH 7.4) saturated with (a) N_2 and air. (b) CVs obtained with the GCE in 0.1 M phosphate buffer (pH 7.4) saturated with N_2 in the presence (red) or absence (black) of 400 μM H_2O_2 . Potential scan rate: 100 mV s^{-1} .

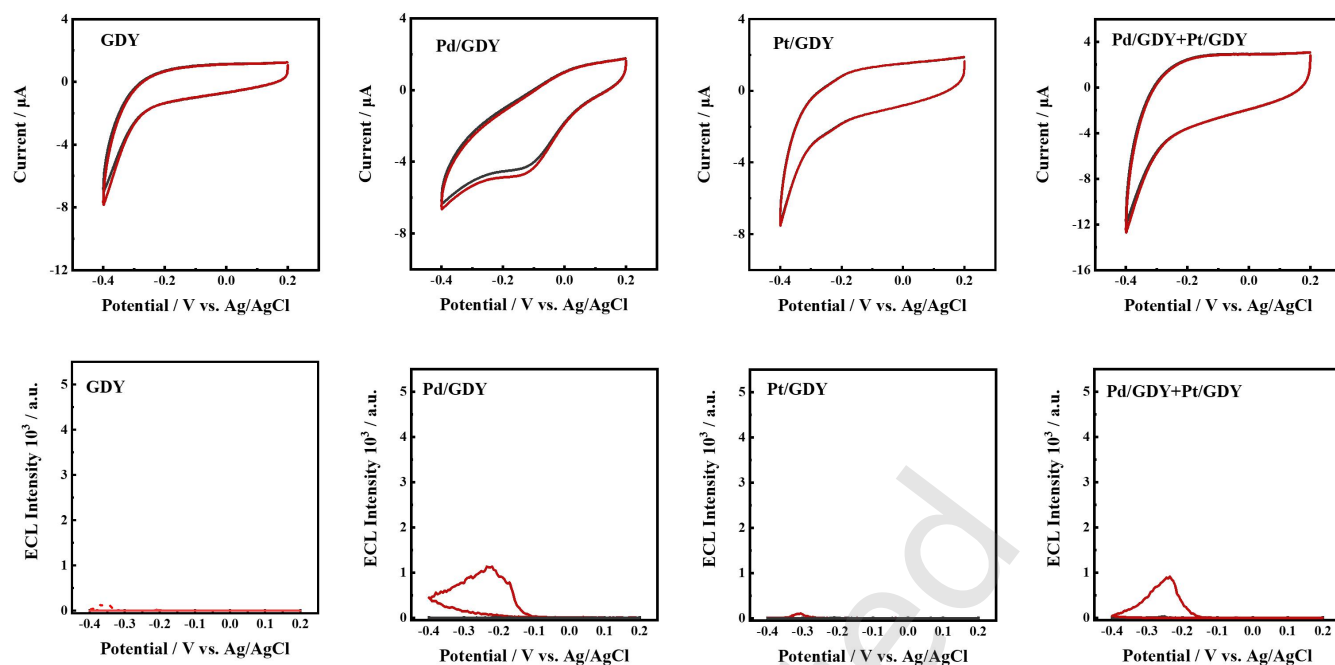


Figure S5. CVs and corresponding ECL-potential curves obtained at GDY/GCE, Pd/GDY/GCE, Pt/GDY/GCE and GCE modified with a physical mixture of Pd/GDY and Pt/GDY in 0.1 M phosphate buffer (pH 7.4) containing 100 μM L-012 with (dotted) or without (solid) 200 μM H_2O_2 . Potential scan rate: 100 mV s^{-1} .

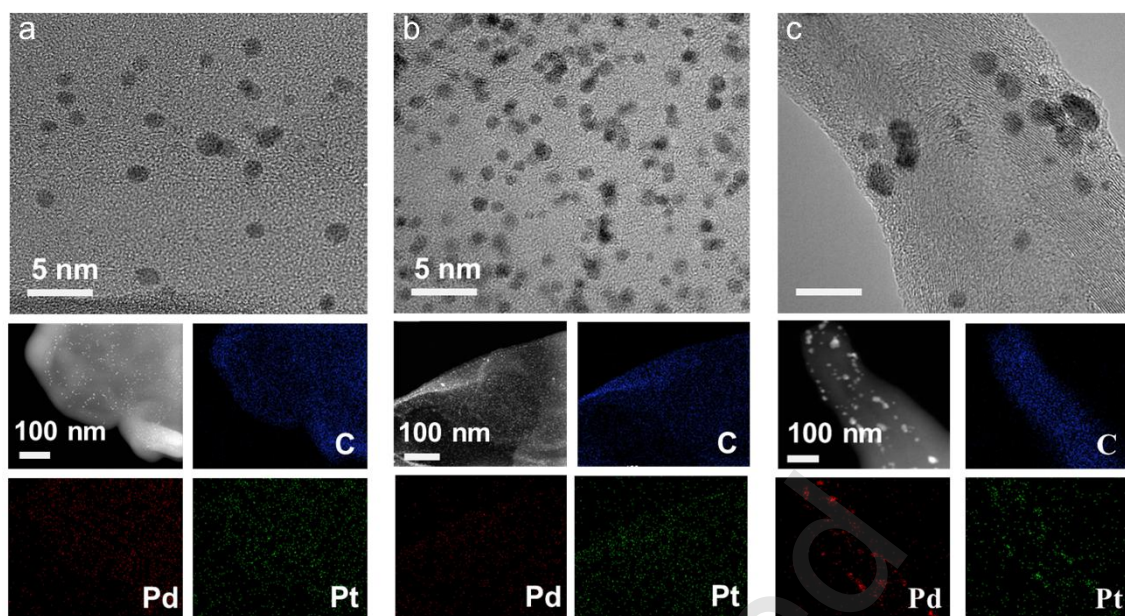


Figure S6. HRTEM image of (a) PdPt/GO, (b) PdPt/GR and (c) PdPt/MCNT and the corresponding mapping of C (blue), Pd (red), and Pt (green).

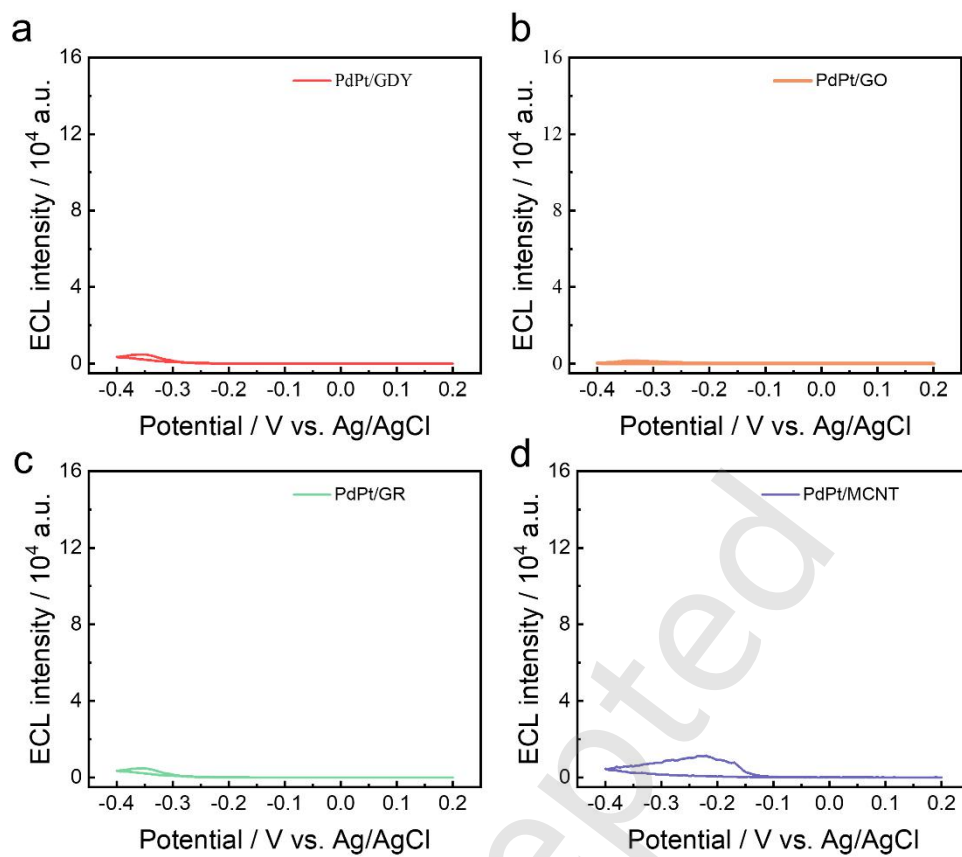


Figure S7. ECL-potential curves of (a) PdPt/GDY-, (b) PdPt/GO-, (c) PdPt/GR-, and (d) PdPt/MCNT-modified GC electrodes in 0.1 M phosphate buffer (pH 7.4) containing 100 μ M L-012.

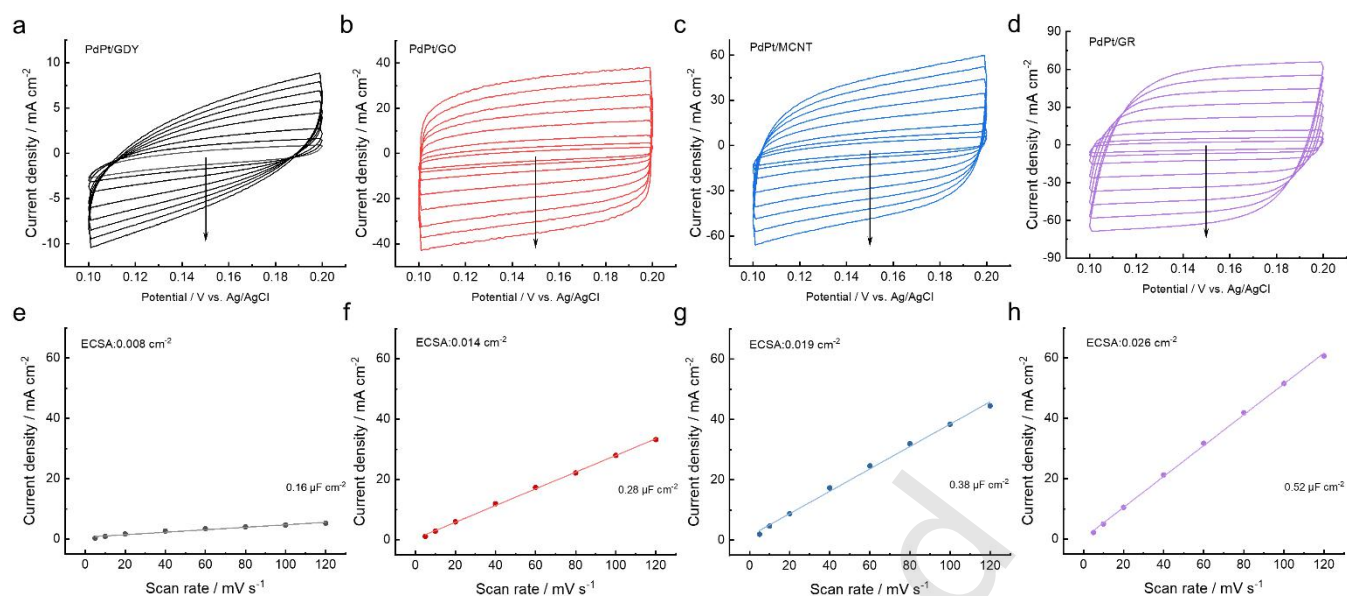


Figure S8. CVs obtained with the (a) PdPt/GDY/GCE, (b) PdPt/GO/GCE, (c) PdPt/MCNT/GCE and (d) PdPt/GR/GCE for HPOR process at scan rates of 5, 10, 20, 40, 60, 80, 100, and 120 mV s⁻¹.

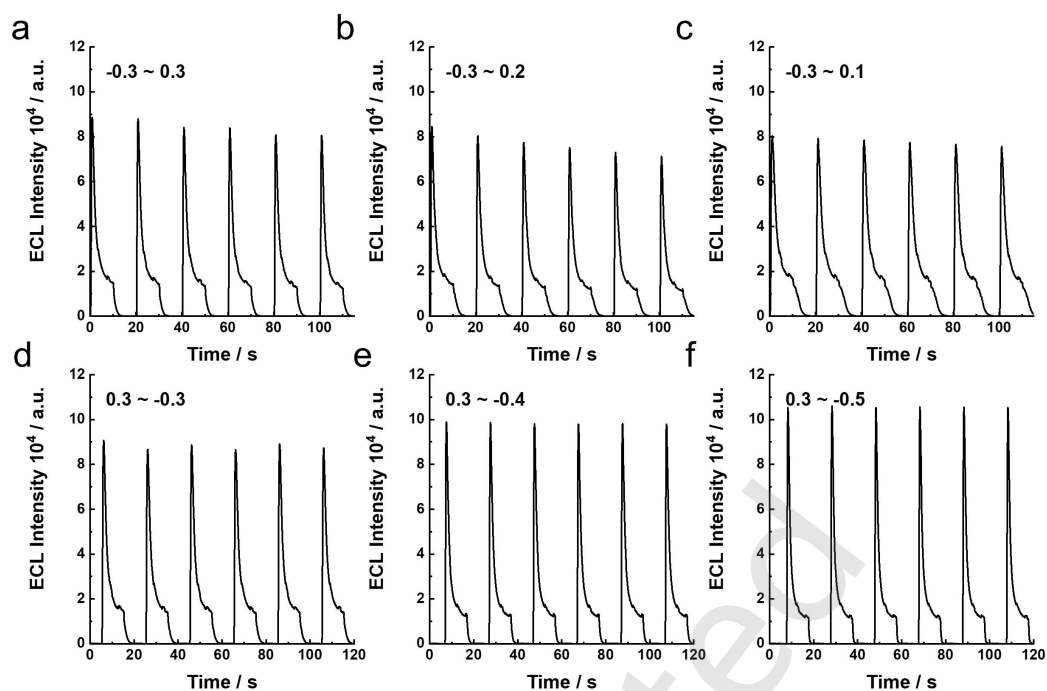


Figure S9. ECL-time curves obtained at PdPt/GDY/GCE in phosphate buffer containing 100 μM L-012 and 200 μM H_2O_2 by stepping pulse from -0.30 V to (a) +0.30 V, (b) +0.20 V and (c) +0.10 V, and from +0.30 V to (d) -0.30 V, (e) -0.40 V, (f) -0.50 V.

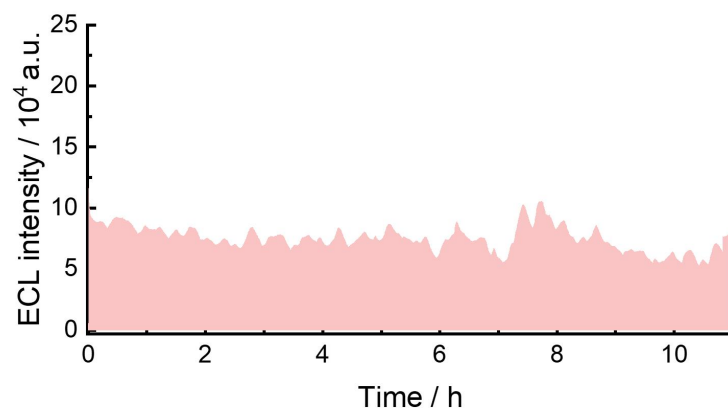


Figure S10. ECL-time curves obtained at the PdPt/GDY/GCE in phosphate buffer containing 100 μM L-012 and 400 μM H_2O_2 under a continuous potential scanning from -0.40 to +0.20 V after electrolysis for 11 h.

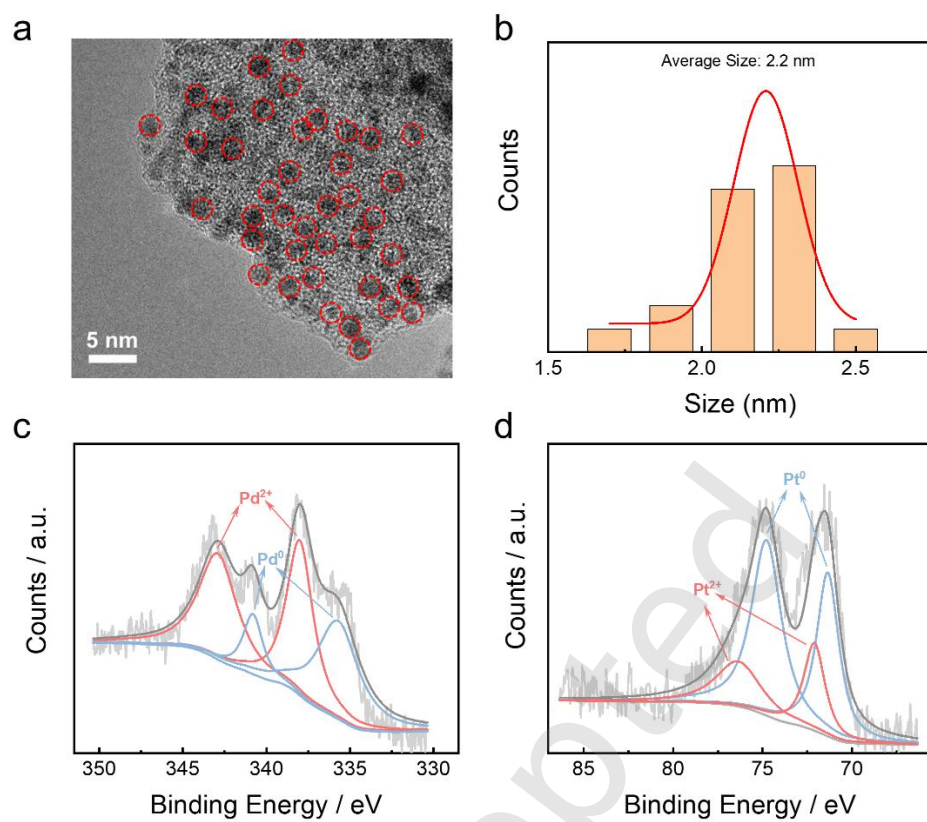


Figure S11. (a) Post-reaction HRTEM image of PdPt/GDY. (b) Size distribution of PdPt nanoparticles on GDY after electrolysis. High-resolution XPS spectra of post-reaction PdPt/GDY: (c) Pd 3d and (d) Pt 4f.

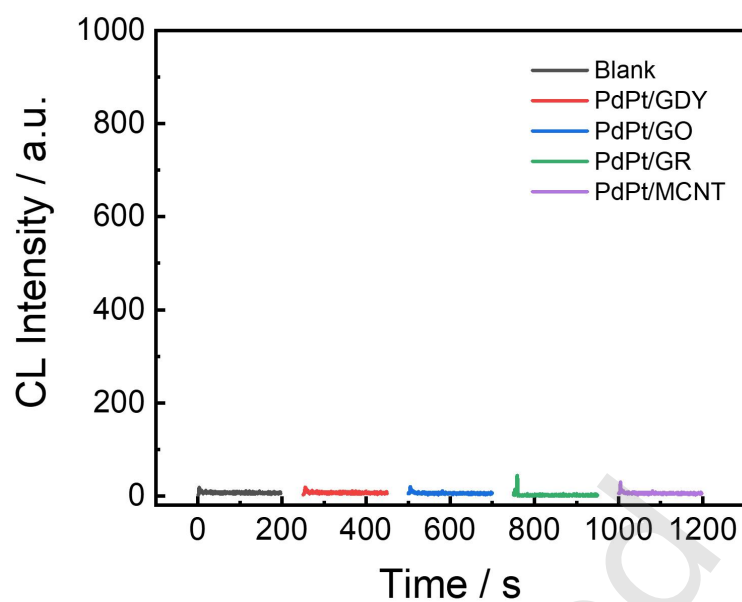


Figure S12. Chemiluminescence signals measured by injecting 100 μM L012 into a 0.1 M phosphate buffer (pH = 7.4) containing 200 μM H_2O_2 and 0.03 mg/mL PdPt/GDY, PdPt/GO, PdPt/GR, and PdPt/MCNT.

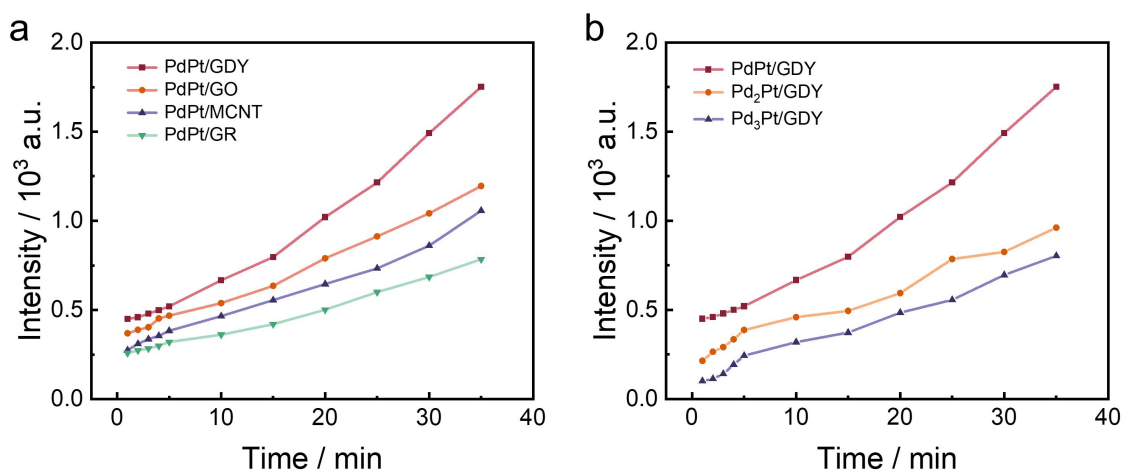


Figure S13. Fluorescence intensity of 0.1 M phosphate buffer containing 5 μ M DCDHF and 200 μ M H_2O_2 for electrolyzing different times using (a) PdPt/GDY-, PdPt/GO-, PdPt/GR-, PdPt/MCNT-modified GC electrodes as well as (b) PdPt/GDY-, Pd₂Pt/GDY-, Pd₃Pt/GDY-modified GC electrodes. The electrode was poised at -0.20 V.

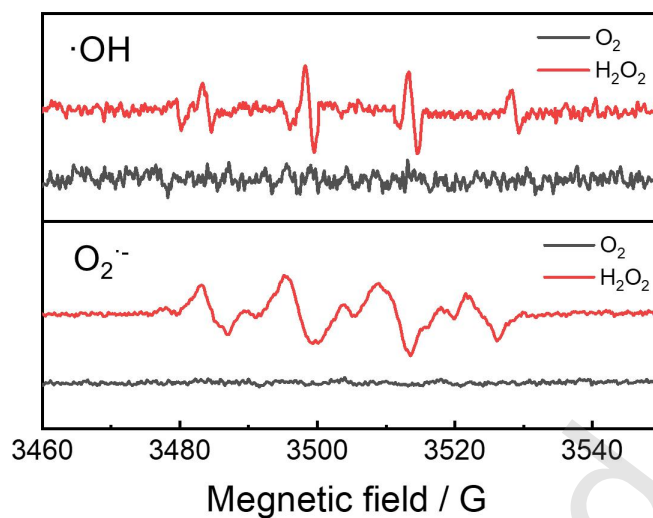


Figure S14. EPR spectra of DMPO- $\cdot\text{OH}$ and DMPO- $\text{O}_2^{\cdot-}$ formed on PdPt/GDY-modified GC electrode in 0.1 M phosphate buffer (pH 7.4) during ORR (gray) and HPOR (red).

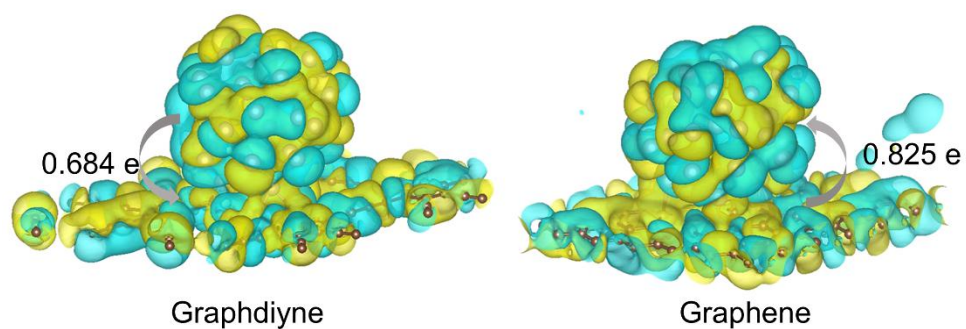


Figure S15. Charge density differences of PdPt/GDY and PdPt/GR. Yellow and blue regions represent the accumulation of negative and positive charge, respectively. The value of isosurface is $4 \times 10^{-7} \text{ e}/\text{\AA}^3$.

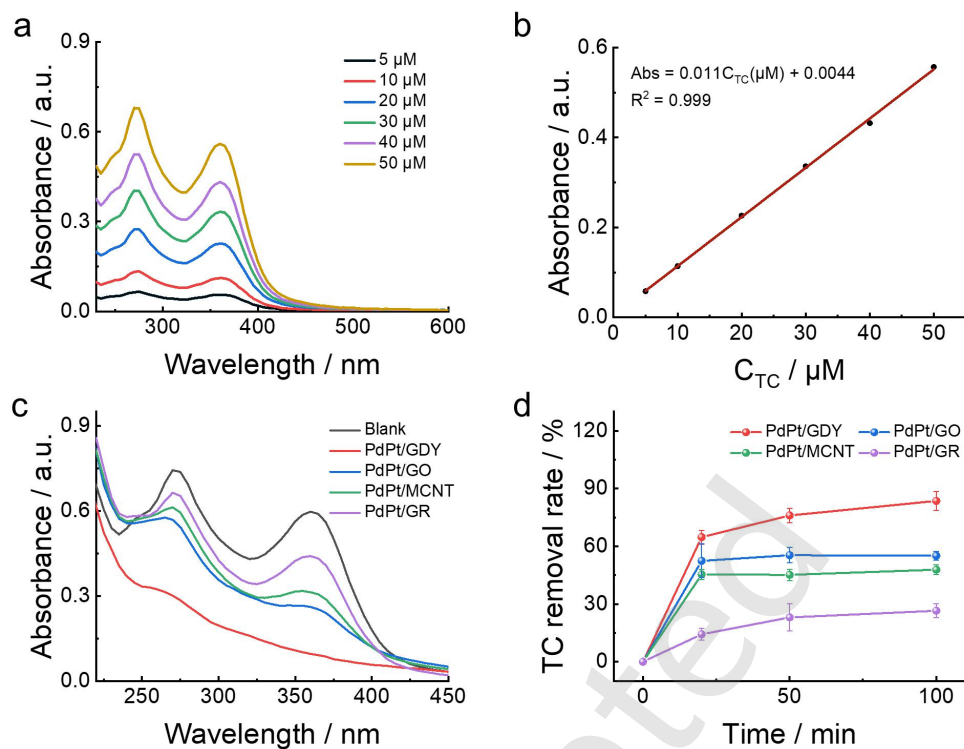


Figure S16. (a) UV-vis absorption spectrum of TC at different concentrations and (b) the linear relationship between UV-vis absorbance and TC concentration. (c) UV-vis absorption spectrum of TC obtained with PdPt/GDY, PdPt/GO, PdPt/MCNT, and PdPt/GR in in 0.5 M Na_2SO_4 containing 200 μM H_2O_2 . The electrodes were poised at -0.30 V for 100 min. (d) TC removal rate obtained with PdPt/GDY, PdPt/GO, PdPt/MCNT, and PdPt/GR in 0.5 M Na_2SO_4 containing 200 μM H_2O_2 . The electrodes were poised at -0.30 V for 100 min.

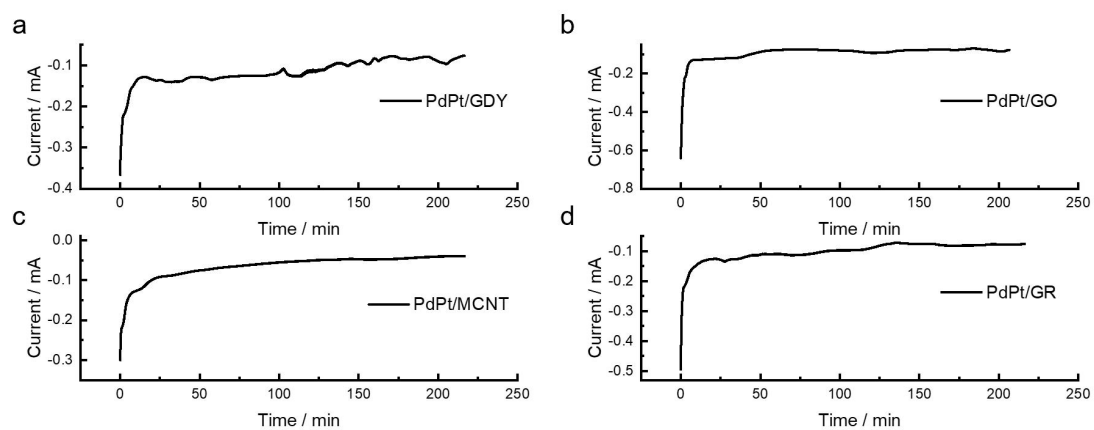


Figure S17. Amperometric current profiles obtained with (a) PdPt/GDY/GCE, (b) PdPt/GO/GCE, (c) PdPt/MCNT/GCE and (d) PdPt/GR/GCE in 0.5 M Na₂SO₄ containing 20 mg L⁻¹ PFOA and 200 μM H₂O₂. The electrodes were poised at -0.30 V for 200 min.

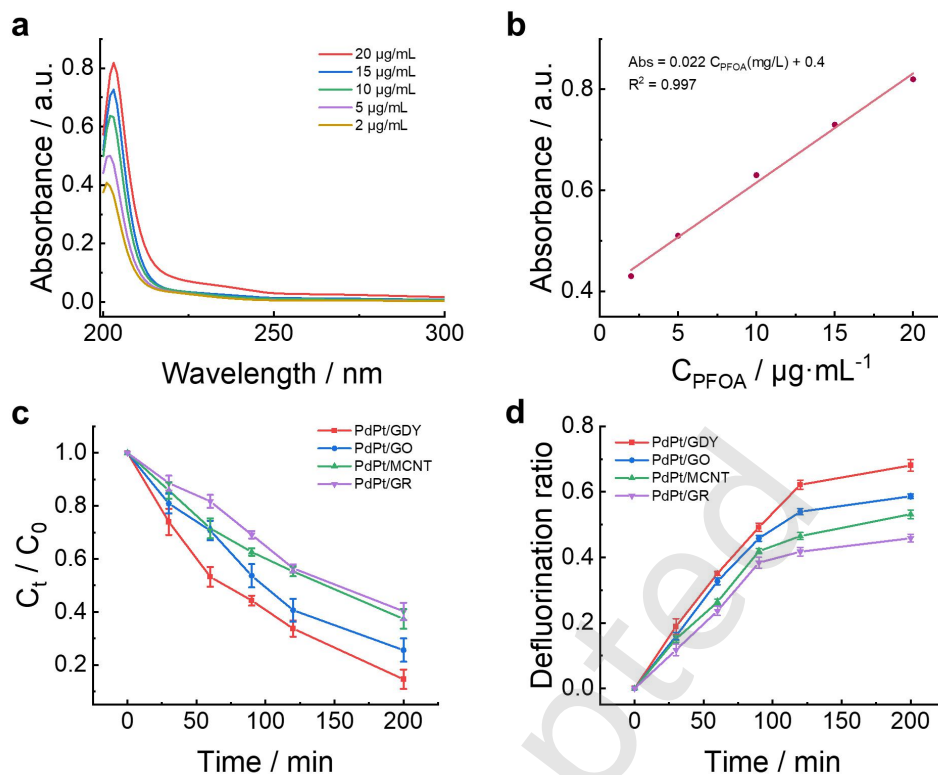


Figure S18. (a) UV-vis absorption spectrum of PFOA at different concentrations and (b) the linear relationship between UV-vis absorbance and PFOA concentration. (c) PFOA degradation rate and (d) defluorination of PdPt/GDY, PdPt/GO, PdPt/MCNT, and PdPt/GR on PFOA in 0.5 M Na_2SO_4 containing 200 μM H_2O_2 . The electrodes were poised at -0.30 V for 200 min.

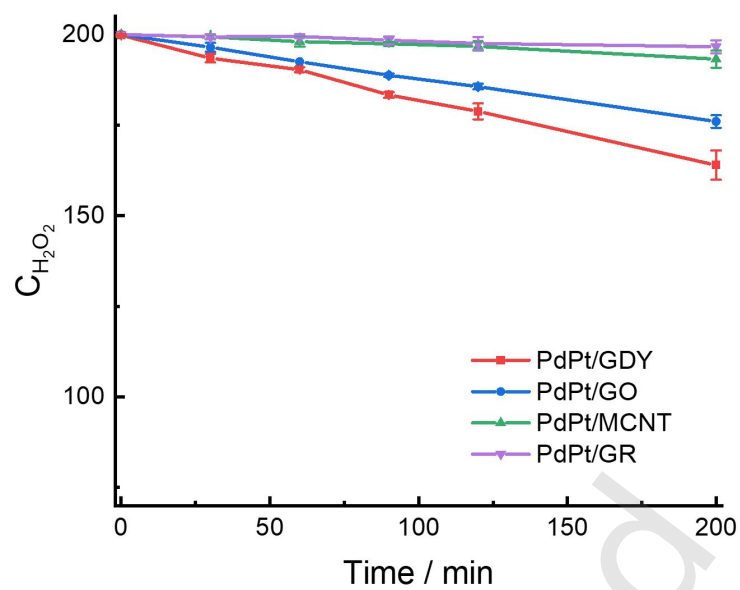


Figure S19. Residual H₂O₂ concentrations obtained with PdPt/GDY, PdPt/GO, PdPt/MCNT, and PdPt/GR during PFOA degradation.

Table S1. Absolute Pd and Pt loadings (wt%) determined by ICP-MS. The subscript for PdPt/GDY represents the nominal concentration of element Pt compared to element Pd.

	Pd (wt.%)	Pt (wt.%)
PdPt/GDY	11.60	13.40
Pd ₂ Pt/GDY	15.34	9.66
Pd ₃ Pt/GDY	19.10	5.90

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