In Situ Spectroelectrochemical Detection of Oxygen Evolution Reaction Intermediates with a Carboxylated Graphene–MnO₂ Electrocatalyst

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Cite This: ACS Appl. Mater. Interfaces 2022, 14, 5177–5182			Read Online	
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ABSTRACT: In electrocatalyst-assisted water splitting, the oxygen evolution reaction (OER) imposes a performance limit due to the formation of different catalyst-bound intermediates and the scaling relationship of their adsorption energies. To break this scaling relationship in OER, a bifunctional mechanism was proposed recently, in which the energetically demanding step of forming the *OOH intermediate, through the attack of a water molecule on the oxo unit (*O, with * representing a reactive metal center), is facilitated by proton transfer to the second catalytic site. This mechanism was supported theoretically but so far by only very few experiments with a proton-transfer agent in basic media. However, active metal-containing catalysts could be destroyed in alkaline media,



raising questions on practical applications. To date, this mechanism still lacks a systematic spectroscopic support by observing the short-lived and limited amount of reactive intermediates. Here, we report an operando Raman spectroscopic observation of the OER intermediates in neutral media, for the first time, via a bifunctional mechanism using a carboxylated graphene– MnO_2 (represented by Gr-C- MnO_2) electrocatalyst. The formation of the Mn–OOH intermediate after the attack of a water molecule on the Mn=O complex is followed by a proton transfer from Mn–OOH to the functionalized carboxylates. The role of the functionalized carboxylates to improve the catalytic efficiency was further confirmed by both pH-dependent and isotope (H/D)-labeling experiments. Furthermore, with a unique strategy of using a hybrid aqueous/nonaqueous electrolyte, the OER was alleviated, allowing sufficient Mn–OOH intermediates for *in situ* Raman spectroscopic observation.

KEYWORDS: oxygen evolution reaction intermediates, Raman spectroscopy, reaction mechanism, graphene-supported manganese oxide, electrochemistry

he oxygen evolution reaction (OER) in electrochemical \bot water splitting is an essential step in the production of renewable fuels, such as hydrogen.¹⁻⁸ The most widely accepted mechanism for metal oxide-catalyzed OER involves four consecutive proton-coupled electron-transfer processes via the formation of multiple electrocatalyst-bound intermediates (e.g., M-OH, M=O, and M-OOH, with M representing a reactive metal center) (Figure S1a of the Supporting Information).^{9,10} The adsorption of these intermediates on M requires an additional energy input (known as overpotential η) to continue the OER process, where the formation of M– OOH via the nucleophilic attack of a water molecule to M=O is regarded as an energetically demanding step. Rossmeisl and co-workers demonstrated that the adsorption energies of these intermediates on the reactive metal center (M) exhibit a strong linear correlation (i.e., scaling relationship), where the difference in the adsorption energies between M-OH and M-OOH keeps constant (3.2 eV) regardless of any electrocatalysts used.¹¹

To overcome the performance limit of this conventional mechanism, a bifunctional mechanism involving two catalytically active sites to work cooperatively was proposed recently (Figure S1b).^{12,13} In the bifunctional mechanism, during the

energetically demanding step of forming M–OOH, while the metal-containing side of M–OOH is supported by the catalyst, the hydroperoxyl side of M–OOH is stabilized by a proton acceptor (which is lacking in the conventional mechanism). Although the direct nucleophilic attack on M=O by H₂O to form M–OOH is energetically unfavorable, a concerted proton transfer to the neighboring acceptor can reduce the energy barrier significantly. To date, theoretical predictions and only a few experimental investigations in basic aqueous media have validated the bifunctional mechanism.^{14–16} However, OER in neutral aqueous media is practically desirable because an electrocatalyst could decompose in a strong alkaline solution.^{17,18}

The design of an efficient bifunctional OER electrocatalyst relies on meticulous determination of the reaction inter-

Received:September 16, 2021Accepted:January 3, 2022Published:January 20, 2022





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Figure 1. (a) Proposed bifunctional mechanism of using Gr-C-MnO₂ as an electrocatalyst in the OER of water splitting in a neutral medium. The Mn active center promotes the OER process by sequential formations of the Mn–OH, Mn=O, and Mn–OOH intermediates, in which the final Mn–OOH is stabilized by a proton transfer to the carboxylate groups functionalized on graphene nanosheets. The crystalline structures of the assynthesized Gr-C-MnO₂ nanosheets are revealed by (b) TEM and (c) HR-TEM images, where the layered Gr-C is underneath MnO₂ nanosheets and the interplanar spacing of 0.26 nm in the MnO₂ (020) lattice is indicated. (d) Raman spectra of a Gr-C-MnO₂ hybrid with its constituents show the major features of the MnO₂ moiety (ν_1 : the out-of-plane Mn–O stretching at ~645 cm⁻¹, ν_2 : the in-plane Mn–O stretching at ~575 cm⁻¹, and ν_3 : the interplanar vibration of MnO₂ nanosheets at ~500 cm⁻¹) and the graphene moiety (the G band of the E_{2g} phonon of sp² carbons at ~1605 cm⁻¹ and the D band of the breathing mode of the *K*-point A_{1g} phonons at ~1350 cm⁻¹). The (e) C 1s XPS and (f) FTIR spectra of Gr-C-MnO₂ are analyzed to confirm that carboxylate groups were functionalized on Gr-C-MnO₂.

mediates to understand the limiting factors in OER. Until now, in situ spectroscopy has achieved little success in identifying the OER intermediates due to their presence of short lifetimes and only in trace amounts.^{19–22} The *in situ* spectroscopic observation of the OER intermediates in a liquid environment is even more laborious.^{23,24} Gray and co-workers suggested that the difficulty in detecting intermediates by operando spectroscopy is associated with the fact that the OER intermediates are outnumbered by both reactants and products. Consequently, they applied nonaqueous media to keep the substrate concentrations low, making operando spectroscopic observation of the reactive intermediates possible.²⁵

Herein, we synthesized carboxylated graphene-MnO₂ nanosheets (referred to as Gr-C-MnO₂, with Gr and C representing graphene and the carboxylate groups functionalized on graphene, respectively, as illustrated in Scheme S1 of the Supporting Information) to be used as an electrocatalyst for OER in neutral aqueous media following the bifunctional mechanism. With Gr-C-MnO₂ in OER, the Mn center promotes the formation of the metal-oxo intermediates and the carboxylate groups stabilize the Mn-OOH complex via a proton transfer (Figure 1a). In previous studies, the poor experimental performance of the Mn-based OER catalysts originates from their low electrical conductivity and limited electrocatalytic surface.^{26,27} In this study, MnO₂ nanosheets were grown on conductive graphene to improve electrical conductivity and enrich electrochemical surface areas. We then employed an aqueous-nonaqueous (acetonitrile, denoted by AcCN) mixture as an electrolyte to hinder substrates (i.e., H_2O) from accessing the active catalyst, thus enhancing the relative amount of intermediates for *in situ* spectroscopic detections. Applying operando Raman spectroscopy with assistance of the H/D isotope effect, we were able to identify the key intermediates (Mn–OH and Mn–OOH) in OER and confirm the reaction mechanism based on these experimental observations.

The transmission electron microscopy (TEM) images of the as-synthesized Gr and Gr-C nanosheets (Figure S2) as well as MnO₂ nanosheets grown on Gr (Figure S3) or Gr-C (Figure 1b) are all quite transparent, indicating their thin-layer structures. The high-resolution (HR)-TEM image of Gr-C- MnO_2 (Figure 1c) reveals the clear MnO_2 (020) lattice with an interplanar spacing of 0.26 nm, but the crystal fringe of Gr-C was not observed.²⁸ In Figure 1d, the Raman spectrum of the $Gr-C-MnO_2$ hybrid includes the signals of birnessite MnO_2 (containing three major features of ν_1 : the out-of-plane Mn–O stretching at ~645 cm⁻¹, ν_2 : the in-plane Mn–O stretching at ~575 cm⁻¹, and ν_3 : the interplanar vibration of adjacent MnO₂ nanosheets at ~ 500 cm⁻¹ with the vibrational analysis presented in Figure S4)²⁹ and Gr films (the G band: the E_{2g} phonon of the sp² carbon atoms at ~1605 cm⁻¹ and the Dband: the breathing mode of the K-point phonons with Alg symmetry at ~ 1350 cm⁻¹).³⁰ Moreover, the carboxylate groups functionalized on Gr-C-MnO2 are evidenced by the characteristic peaks of carboxylic C-O and C=O in the C 1s (Figure 1e)³¹ and O 1s (Figure S5)³² X-ray photoelectron spectroscopy (XPS) spectra; in contrast, no such signals exist in the

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Figure 2. (a) LSV plots were scanned at 20 mV s⁻¹ up to the current density of 10 mA cm⁻², showing the required overpotentials of 0.48, 0.38, 0.32, and 0.26 V, respectively, for the Gr-C, MnO_2 , Gr- MnO_2 , and Gr-C- MnO_2 electrodes used in OER. The OER activities of the Gr- MnO_2 and Gr-C- MnO_2 electrodes were further investigated by LSV measurements (b) at different pH from 7.5 to 9 and (c) in the electrolyte of 0.5 M Na_2SO_4 in H_2O and D_2O , respectively, to test proton diffusion kinetics on the electrolyte/catalyst interface. Each experiment in (c) was measured three times. The scale of the plots is enlarged on the right panels to show distinctive curves.



Figure 3. (a) Tafel plot of the Gr-C-MnO₂-assisted OER in 0.5 M Na₂SO₄ was obtained with a scan rate of 2 mV/s. The four linear regions, step A (0-0.81 V), step B (0.81-1.04 V), and steps C + D (1.04-1.54 V) versus RHE, together with the onset of the water oxidation indicate different reaction kinetics involved in the formations of distinctive intermediates. (b) Reaction intermediates are proposed in the Gr-C-MnO₂-assisted OER process. (c) Using the Gr-C-MnO₂ electrocatalyst in a mixed electrolyte of 0.5 M Na₂SO₄ in AcCN/H₂O (5:1), the *in situ* Raman spectra were scanned at 300–750 cm⁻¹ (covering the Mn–O stretching region) with a stepwise increase of the electrochemical potential up to 1.59 V. (d) The *in situ* Raman spectra were scanned at 1000–1500 cm⁻¹ to search for the O–O stretching of the Mn–OOH intermediate with the same experimental conditions of (c), except using MnO₂ alone as an electrocatalyst. (e,f) H/D isotope effect was tested with the same experimental conditions as those of (c,d), respectively, except that 0.5 M Na₂SO₄ dissolved in the mixed electrolyte of AcCN/H₂O (5:1) in (c,d) was replaced with AcCN/D₂O (5:1) in (e,f).

XPS spectrum of Gr-MnO₂ (Figure 1e). In the Fouriertransform infrared (FTIR) spectrum of Gr-C-MnO₂ (Figure 1f), the stretching vibrations of carboxylic C==O and C-O at ~1727 and ~1397 cm⁻¹, respectively, but not in Gr-MnO₂, further validate the carboxylate groups functionalized on Gr-C-MnO₂.³² To determine the effect of carboxylate functionalization on the surface area of MnO₂ in Gr-MnO₂ or Gr-C-MnO₂, we performed the Brunauer–Emmett–Teller (BET) surface area analysis as shown in Figure S6. The BET specific surface areas of Gr-MnO₂ and Gr-C-MnO₂ were calculated to be 104.6 and 105.4 m²/g, respectively. These results signify that the carboxylate functionalization did not significantly change the surface area of MnO₂ in Gr-C-MnO₂ from Gr-MnO₂. The cyclic voltammetry (CV) and impedance spectra (Figure S7) demonstrate that MnO_2 -decorated Gr nanosheets improved the electrocatalytic performance of Gr-C-MnO₂ by increasing electrochemical active surface areas (Figure S8) and electrical conductivity. From a linear sweep voltammetry (LSV) plot (Figure 2a), Gr-C-MnO₂ of higher electrochemical activity required lesser overpotential for OER than Gr-MnO₂. The OER activities of Gr-C-MnO₂ and Gr-MnO₂ were compared in a basic medium, where OH⁻ acts as a proton acceptor. Figure 2b shows that the OER efficiency changes more significantly in Gr-MnO₂ than in Gr-C-MnO₂ as the pH value increases. This is because the deprotonation of Mn–OOH in Gr-C-MnO₂ was assisted with the carboxylate group

(as illustrated in Figure 1a), resulting in less pH-dependent OER efficiency, which is similar to the previous report of a phosphate-functionalized perovskite.^{15,33} To further verify the proton transfer by the carboxylate group, we performed the OER in D₂O solution using the same bifunctional Gr-C-MnO₂ electrocatalyst. The mobility of the deuteron is slower than that of the proton;³⁴ accordingly, the use of the D₂O electrolyte can effectively slow down the proton transfer in OER kinetics. As shown in Figure 2c, the LSV current decreases apparently with the Gr-MnO₂ electrocatalyst operating in D₂O, whereas no significant LSV current changes by replacing Gr-MnO₂ with Gr-C-MnO₂. This outcome further signifies that the carboxylate group in Gr-C-MnO₂ accelerated the proton-transfer process, resulting in a weak H/D isotope effect.

We attempted to observe the reaction intermediates involved in the Gr-C-MnO2-assisted OER by in situ Raman spectroscopy. In Gr-C-MnO₂-assisted OER experiments in 0.5 M Na₂SO₄ electrolyte, a blue shift of the ν_1 band and minor red shifts of the ν_2 and ν_3 bands of MnO₂ were observed as the electrochemical potential was increased from 0 to 1.59 V (Figure S12), whereas the D and G bands of graphene did not show apparent shifts (Figure S13). The signal shifts in the $\nu_1 - \nu_3$ bands of MnO₂ are associated with the intercalation/ deintercalation of electrolytic ions during the potential cycling as reported earlier³⁵ and discussed in Section F.1 of the Supporting Information To prove that these spectral shifts (Figure S12) originated from the aqueous electrolyte, we replaced the aqueous electrolyte with AcCN or toluene to show no peak shifts during the electrochemical process (Figure S14).

As discussed earlier, the difficulty of detecting short-lived reaction intermediates on highly active electrodes in operando experiments comes from the overwhelming substrate concentration. We addressed this challenge to lower the substrate concentration by using 0.5 M Na₂SO₄ in a mixed electrolyte of $AcCN/H_2O = 5:1$. Before performing this experiment, we investigated the effect of AcCN on OER by conducting the CV measurement with AcCN alone as an electrolyte (Figure S9). The low current without any redox signal in the CV scan indicates that AcCN does not contribute to OER. In Figure S10, we compared the LSV scans using a $Gr-C-MnO_2$ electrocatalyst in the electrolyte of 0.5 M Na₂SO₄ in water and AcCN/H₂O, respectively, to examine the role of AcCN in our reaction system. The addition of AcCN in water decreases the OER current in LSV, indicating that AcCN slows down the OER reaction as reported in the literature.²⁵ With this mixed electrolyte, a Tafel plot in Figure 3a (with a representative LSV plot displayed in Figure S11) indicates four linear regions together with the onset of water oxidation, step A (0-0.81 V), step B (0.81-1.04 V), and steps C + D (1.04-1.54 V), suggesting the formations of distinctive intermediates (Figure 3b). Prior to in situ Raman spectroscopy experiments, we conducted chronoamperometric tests in the Gr-C-MnO2assisted OER to optimize the excitation laser and signal acquisition systems (Section F.2 and Figures S15-S17 of the Supporting Information).

The Raman spectra of Figure 3c exhibit a new band at \sim 360 cm⁻¹ (corresponding to the Mn–O stretching of the Mn–OH intermediate in step B of Figure 3b).³⁶ This peak started growing at \sim 0.84 V, reaching its maximum at \sim 0.99 V and then decreasing and vanishing at \sim 1.49 V. On the other hand, another new signal at 614.8 cm⁻¹ appeared at >1.09 V (Figure

3c), corresponding to the Mn–O stretching of the Mn–OOH intermediate (step D of Figure 3b). Despite the difficulty of discerning this new signal in the very crowded region at 550-700 cm⁻¹, we identified it at \sim 614.8 cm⁻¹ by very careful spectral deconvolution (see the detailed analysis in Figure S18). To confirm that the signal at ~614.8 cm⁻¹ is related to the Mn–OOH intermediate, we further looked for the signal of the peroxide bond (O-O) stretching at >1000 cm⁻¹. However, to mitigate the severe interference from the strong Raman signals of graphene at $1200-1700 \text{ cm}^{-1}$ (Figure S13), we employed only MnO_2 (rather than Gr-C-MnO₂) as an electrocatalyst to conduct the OER experiment, despite the much lower electrocatalytic activity by using MnO₂ alone. As evidenced in Figure 3d, the peak at 1354 cm⁻¹, corresponding to the O-O stretching of the Mn-OOH intermediate, indeed showed up when the potential was applied at $\sim 1.09 - 1.49$ V.

Additionally, the H/D isotope effect was used to confirm the spectroscopic observations of the Mn-OH and Mn-OOH intermediates. Comparing Figure 3c with Figure 3e, a red shift of the Mn-O stretching signal from 360 to 351 cm⁻¹ was observed after Mn-OH was deuterated to Mn-OD; nevertheless, both signals (at 360 and 351 cm⁻¹) appeared in the same potential range of ~0.84-1.49 V. Similarly, in Figure 3d,f, the O–O stretching of Mn–OOH at 1354 cm⁻¹ is shifted to 1342 cm⁻¹ of Mn-OOD, but again, both signals (at 1354 and 1342 cm⁻¹) showed up in the same \sim 1.09–1.49 V interval. These prominent red shifts in both the Mn-O stretching of Mn-OH and the O-O stretching of Mn-OOH after the deuteration of the intermediates (to Mn-OD and Mn-OOD) can be attributed to the primary kinetic isotope effect. In contrast, the Mn-O stretching of Mn-OOH experienced a small red shift from 614.8 to 613.2 cm⁻¹ in Mn-OOD (Figure S19). In Mn-OOH, H is not attached directly to the Mn-O bond. Thus, replacing H with D has less effect on the Mn-O stretching, which is ascribed to the secondary kinetic isotope effect.

In conclusion, we present a highly efficient Gr-C-MnO₂ electrocatalyst to assist the OER of water splitting in neutral media. The Gr-C-MnO₂-assisted OER via a bifunctional mechanism can be developed based on our experimental evidence. The reaction starts from binding a H₂O with the Mn active center to generate $Mn-OH_2$ (step A in Figure 3b). At electrochemical potentials >0.81 V, the removal of H⁺ from Mn-OH₂ leads to the formation of a hydroxo-ligand (Mn-OH, step B in Figure 3b), which is evidenced by the Raman signal of 360 cm⁻¹ (the Mn–O stretching of Mn–OH).³⁶ The successive ejection of H⁺ materializes a very short-lived oxointermediate (Mn=O, step C in Figure 3b).³⁷ At >1.09 V, the nucleophilic attack of H₂O on Mn=O creates Mn-O-OH₂ and the subsequent H⁺ release renders a hydroperoxy-ligand (Mn–OOH, step D in Figure 3b), which is responsible for the observed Raman signals at 614.8 and 1354 cm⁻¹ (the Mn-O and O-O stretchings of Mn-OOH, respectively). Finally, with the simultaneous releases of H⁺ and O₂, the active metal center (Mn) returns to its initial state surrounded by H2O $(Mn-OH_2)$, step A in Figure 3b). In our experiments, the existence of the Mn-OH and Mn-OOH intermediates was evidenced by operando Raman spectroscopic observations and confirmed with the H/D isotopic tests. The functionalized carboxylate groups in Gr-C-MnO₂ to improve OER activity were examined by both pH-dependent and H/D isotopic experiments. This research not only gains insight into the fundamental water-oxidation mechanism but also provides

electrochemical tests for an artificially designed water-oxidizing catalyst.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c17909.

Conventional and bifunctional mechanisms of metal oxide electrocatalyst-assisted water splitting; experimental section; spectroscopic and electron microscopic characterizations; fabrication of the as-synthesized electrocatalyst-based electrodes; electrochemical measurements; and operando Raman spectroelectrochemical investigation (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported, in part, by the Ministry of Science and Technology (MOST) of Taiwan under Grant no. 110-2113-M-002-017.

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Supporting Information

In Situ Spectroelectrochemical Detection of Oxygen Evolution Reaction Intermediates with a Carboxylated Graphene-MnO₂ Electrocatalyst

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A. Conventional and bifunctional mechanisms of metal oxide electrocatalysts-assisted water splitting



Figure S1. A comparison of the conventional and bifunctional mechanisms of the oxygen evolution reaction (OER) in water splitting performed in neutral medium. (a) A conventional mechanism in the metal oxide-catalyzed OER involves four consecutive steps, in which the metal atom (represented by M) acts as an active catalytic center. The OER process begins with the electrophilic attack of a water molecule on M, rendering the M-OH intermediate after releasing a proton. The M-OH transforms to M=O by removing another proton. The subsequent electrophilic attack of another water molecule on M=O yields the M-OOH intermediate accompanied with a proton ejection. Finally, a proton and an oxygen molecule are released from M-OOH; meanwhile, the active catalytic center returns to its original state (M). (b) Comparatively, the processes in a bifunctional mechanism are the same as those of the conventional mechanism up to the formation of the M=O intermediate. However, the bifunctional mechanism involves two catalytic active centers to work cooperatively, involving a reactive metal center (M) and a proton acceptor (A⁻). For example, the two catalytic active centers in this study include the Mn atom of MnO₂ acting as the reactive metal center (M = Mn) and the carboxylate groups modified on graphene nanosheets serving as the proton acceptor ($A^- = COO^-$). During the attack of a water molecule on M=O, while the catalytic center (M) provides an active site to form a metal-oxo intermediate (M-OOH), the proton acceptor (A⁻) helps to stabilize the hydroperoxyl side of M-OOH.

B. Experimental Section

B.1. Chemicals: Graphite (natural, 99.9995%), sulfuric acid (H₂SO₄, ACS, 95.0–98.0%), and potassium permanganate (KMnO₄, ACS, 99.0%) were purchased from Alfa Aesar. Sodium nitrate (NaNO₃, ACS, 99.5%), sodium carbonate (Na₂CO₃, anhydrous grade for analysis, 99.9%), sodium hydroxide solution (NaOH, Titrisol, 1 M), and hydrogen chloride (HCl, reagent grade for analysis, 37%) were obtained from Merck. Benzyl alcohol and benzaldehyde were procured from Sigma. N-methyl-2-pyrrolidone (NMP) was supplied from Alfa Aesar. Acetonitrile (CH₃CN, 99.5%, denoted hereafter by AcCN) was obtained from Merck. All the chemicals used in this study were of analytical reagent grade and used without further purification.

B.2. Solution-based syntheses of electrocatalysts

Synthesis of graphene nanosheets

The synthesis of graphene nanosheets was carried out with a modified Hummer's method. S1-S2 Graphite flakes (2 g), NaNO₃ (2 g), and H₂SO₄ (90 ml, 98%) were mixed (Scheme S1a) in a 1000 ml volumetric flask and kept at an ice bath (0-5 °C) with continuous stirring. The mixture was stirred for 4 hr at this temperature and KMnO₄ (12 g) was added very slowly to the suspension. The rate of addition was controlled carefully to keep the reaction temperature lower than 15 °C. The mixture was diluted very slowly by adding 184 ml water and kept stirring for 2 hr. The ice bath was then removed and the mixture was stirred at 35 °C for 2 hr. The above mixture was kept in a reflux system at 98 °C for 10–15 min. Afterwards, the solution was cooled to 30 °C and turned to brown color, followed by another 10 min cooling to 25 °C and keeping the temperature for 2 hr. The solution was finally treated with 40 ml H₂O₂ to change the color to bright yellow. An equal amount of the solution was added to two separate beakers containing 200 ml water and stirred for 1 hr. Then, stopped stirring and waited for 3-4 hr. Particles started to form at the bottom of the beaker. By pouring the solution into a filter to remove the remaining water, the resulting mixture was washed repeatedly by centrifugation with 10% HCl and then with deionized (DI) water several times until a gel-like product (pH-neutral) was formed. Finally, the substrate was dispersed in water and sonicated for 1 hr to obtain graphene nanosheets.

Synthesis of carboxylated graphene nanosheets

Carboxylated graphene (Gr-C) nanosheets were synthesized by activating the as-produced graphene sample with chloroacetic acid (ClCH₂CO₂H). In a typical process (**Scheme S1a**), ClCH₂CO₂H, NaOH, and graphene oxide were added to DI water and then sonicated for 3 hr to speed up the elimination of NaCl. The resulting Gr-C solution was neutralized by HNO₃ and purified with acetone and water for several times.

Synthesis of MnO₂ nanosheets

Thin-layered birnessite MnO₂ nanosheets were synthesized with a two-phase solution-based approach as illustrated in **Scheme S1b**. First, a mixture of water and benzyl alcohol (7:1) was stirred at 800 rpm in room temperature. Because benzyl alcohol is immiscible with water, benzyl alcohol was developed as small micro-spheres/bubbles inside water. Subsequently, aqueous KMnO₄ was added dropwise to the reaction mixture to oxidize benzyl alcohol to benzaldehyde; meanwhile, KMnO₄ was reduced to MnO₂. Since this redox reaction occurred on the surfaces of the micro-spheres/bubbles of benzyl alcohol, MnO₂ was formed as nanosheets on these emulsions.

Synthesis of a Gr-C-MnO₂ hybrid

The process to produce $Gr-C-MnO_2$ (Scheme S1) is the same as that to synthesize MnO_2 nanosheets. During the synthesis, aqueous Gr-C and aqueous $KMnO_4$ were added to a mixture of water and benzyl alcohol, which were then stirred for 6 hr. The resultant product was separated by centrifugation and washed several times with DI water. Finally, the product was dried at 80 °C for 12 hr.



Scheme S1. The preparation of a carboxylated graphene- MnO_2 hybrid (represented by Gr-C- MnO_2). (a) A schematic process illustrates the synthesis of graphene (Gr) nanosheets, followed by functionalizing carboxylate groups on the graphene surface (denoted by Gr-C). Subsequently, MnO_2 nanosheets were growth on Gr-C to form a Gr-C- MnO_2 hybrid. (b) Schematic illustration of a two-phase solution-based method for the synthesis of MnO_2 nanosheets, Gr- MnO_2 , and Gr-C- MnO_2 .

C. Spectroscopic and electron microscopic characterizations

Instrumentation: Raman spectra of the as-synthesized electrocatalysts were recorded in a confocal Raman microscope (NT-MDT, NTEGRA Spectra) equipped with a 1800 g mm⁻¹ grating and a 488 nm laser as an excitation source. A Fourier-transform infrared (FTIR) spectrophotometer (Horiba, FT720) was employed to identify the functional groups of the as-synthesized electrocatalytic compounds. X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCA photoelectron spectrometer (Ulvac-PHI 1600) with the photon energy of 1486.6 ± 0.2 eV (Al Ka radiation). The binding energies of the observed signals were calibrated against the carbon C 1s peak at 284.8 eV. The Shirley-Sherwood method was employed to subtract the background. With the Brunauer-Emmett-Teller (BET) method, surface areas were analyzed using a Quantachrome Autosorb-6 instrument. For the BET analysis, the samples to be tested were degassed at 150 °C for 12 hr and subjected to nitrogen gas adsorption-desorption. High-resolution transmission electron microscopy (HR-TEM) was conducted in a transmission electron microscopy (JEOL, JEM-2100F) with an operating voltage of 200 kV.



Figure S2. TEM images of the as-synthesized (a) graphene (Gr) nanosheets and (b) carboxylated graphene (Gr-C) nanosheets. The transparent TEM images indicate the thin-layered structures of the Gr and Gr-C nanosheets.



Figure S3. A TEM image of the as-synthesized Gr-MnO₂ displays a graphene (Gr) film is covered by island-like MnO₂ nanosheets.



Figure S4. (a) The Raman spectrum of birnessite MnO₂ nanosheets includes three major vibrational features of the v_1 band (the out-of-plane Mn-O stretching) at ~645 cm⁻¹, the v_2 band (the in-plane Mn-O stretching) at ~575 cm⁻¹, and the v_3 band (the interplanar vibration of adjacent MnO₂ nanosheets) at ~500 cm⁻¹. The motions of the v_1 , v_2 , and v_3 vibrations are identified and illustrated as follows. (b) In the birnessite MnO₂ structure, the octahedral [MnO₆] moieties interconnect each other through the edge sharing to form a 2D layered structure. The v_1 band can be identified as the symmetric stretching (A_{1g}) of the Mn-O bond along the d_{x²-y²} orbital in the octahedron of [MnO₆]. The v_2 band is attributed to the Mn-O stretching along the d_{x²-y²} orbital in the basal plane of the [MnO₆] sheet. (c) The v_3 band is a relatively weak vibrational mode, corresponding to the interplanar vibration of adjacent layers in MnO₂ nanosheets, of which the vibrational frequency is closely related to the extent of the layer spacing.



Figure S5. The O 1s XPS spectrum of the as-synthesized $Gr-C-MnO_2$ was observed and deconvoluted for spectral analysis. The Mn-O bond of MnO_2 nanosheets and the C-O bond of the carboxylic group are responsible for the observed XPS signals with their binding energies of 529.6 eV and 531.1 eV, respectively.



Figure S6. In the BET specific surface area measurements, the N_2 isotherm adsorption-desorption analyses of (a) Gr-MnO₂ and (b) Gr-C-MnO₂ reveal the specific surface areas of Gr-MnO₂ and Gr-C-MnO₂ to be 104.6 and 105.4 m²/gm, respectively.

D. Fabrication of the as-synthesized electrocatalysts-based electrodes

The working electrodes were fabricated by depositing catalyst inks on a rectangle-shaped carbon cloths $(1 \times 4 \text{ cm}^2)$ using a drop-drying method at ambient temperature. The catalyst inks were prepared by sonicating the as-synthesized electrocatalyst compound for 10 min in isopropyl alcohol. Prior to deposition, the carbon clothes were sequentially cleaned in acetone, 1M HCl solution, DI water, and ethanol under sonication for 15 min each, and then dried. The electrocatalyst was loaded to carbon cloth $(1 \times 1 \text{ cm}^2)$ prior to all electrochemical measurements. The electrocatalyst was of ~0.8 mg on each carbon cloth $(1 \times 1 \text{ cm}^2)$, which was determined by measuring the weight of the carbon cloth before and after the catalyst loading.

E. Electrochemical measurements

E.1. Electrochemical characterization

To evaluate the electrochemical properties of the as-fabricated electrodes for water splitting in 0.5 M Na₂SO₄, a three-electrode system, including the as-synthesized electrocatalyst as a working electrode, a Pt wire as a counter electrode, and a saturated calomel electrode (SCE) as a reference electrode, was employed for measurements with an Autolab potentiostat/galvanostat electrochemical workstation. All electrochemical measurements were repeated twice with a new working electrode. The experimental reproducibility was found very well by using the as-prepared working electrodes. In **Figure S6**, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out using the as-synthesized Gr-C-MnO₂, MnO₂, and Gr-MnO₂ electrocatalysts, respectively, as a working electrode to compare their electrochemical performance.



Figure S7. The electrochemical properties of Gr-C, MnO₂, Gr-MnO₂, and Gr-C-MnO₂ were characterized in a three-electrode cell with 0.5 M Na₂SO₄ aqueous electrolyte, of which the electrochemical cell comprised a Ag/AgCl reference electrode, a Pt counter electrode, and each of the as-synthesized electrocatalysts as a working electrode. (a) The CV measurements were scanned at 5 mV/s between 0 and 1.2 V. All of these samples show their main capacitive nature at 0–0.9 V, resulting from the charge storage processes of MnO₂ and graphene. The improved electrochemical efficiencies of Gr-MnO₂ and Gr-C-MnO₂ are evidenced by their larger integrated areas than those of MnO₂ and Gr-C. Above 0.9 V, the measured currents due to OER exhibit an increasing order of Gr-C < MnO₂ < Gr-MnO₂ < Gr-C-MnO₂. The higher current by using Gr-C-MnO₂ than Gr-MnO₂ signifies that the additional carboxylate groups functionalized on Gr-C-MnO₂ improve the OER efficiency significantly. (b) The Nyquist plots of impedance spectra were carried out in a frequency range from 0.1 Hz to 1 MHz. In the high-frequency region of the Nyquist plot, both the intercept of the obtained spectra with the real axis (Z') and the semi-circular diameter

follow an increasing order of $Gr-C < Gr-MnO_2 \sim Gr-C-MnO_2 < MnO_2$ (with an enlarged image shown in the inset).

E.2. Electrochemical active surface area (EASA)

In **Figure S7**, the higher electrochemical activity of $Gr-C-MnO_2$ than that of MnO_2 can be attributed to the larger active surface area of $Gr-C-MnO_2$, resulting from the composite formation of the layered MnO_2 and graphene nanosheets.



Figure S8. The CV curves using the (a) Gr-C-MnO₂, (c) Gr-MnO₂, and (e) MnO₂ electrocatalysts were measured at different scan rates in 0.5 M Na₂SO₄ electrolyte. The current density vs. scan

rate plots are presented, in which the current density was taken in the non-faradic region of CV at 0.94 V using (b) Gr-C-MnO₂ and (d) Gr-MnO₂ electrocatalysts and at 1.14 V using (f) MnO_2 electrocatalyst.

Determination of EASA

The EASA for an electrocatalyst was estimated from the electrochemical double-layer capacitance. The electrochemical capacitance was determined by measuring the non-faradaic capacitive current associated with the double-layer charging from the scan-rate dependence of CVs.^{S3} The EASA of an electrocatalyst is calculated from the double-layer capacitance,

$$EASA = C_{dl}/C_s$$

where C_{dl} is the capacitance of an electrochemical double-layer and C_s is the specific capacitance of the electrocatalyst (or the capacitance of an atomically smooth planar surface of the electrocatalyst per unit area under identical electrolytic conditions). Although ideally, one would synthesize smooth, planar surface of each electrocatalyst to measure C_s and estimate the EASA, this is not practical for most electrodeposited systems. Here, according to the literature reports about carbon-based electrodes, we took $C_s = 0.02 \text{ mF/cm}^2$ for the EASA calculation. The doublelayer charging current (i_c) equals to the product of the scan rate (v) and the electrochemical doublelayer capacitance (C_{dl}),

$i_c = v C_{dl}$.

Therefore, a plot of i_c as a function of v yields a straight line with the slope of C_{dl} . The EASA was converted from cm² to m²/g by dividing the mass loading of the electrocatalyst. With these calculations, the ESCAs of Gr-C-MnO₂, Gr-MnO₂, and MnO₂ were calculated to be 9.2 m², 9.1 m², and 3.2 m², respectively.



Figure S9. The CV measurement was performed using a $Gr-C-MnO_2$ electrocatalyst in AcCN, with or without Na₂SO₄. The scan rate of 100 mV/sec was performed in the measurements.



Figure S10. The LSV measurement by using a Gr-C-MnO₂ electrocatalyst in the electrolyte of 0.5 M Na₂SO₄ without AcCN (i.e., in pure H₂O) or with AcCN:H₂O (5:1). The scan rate of 2 mV/sec was performed in the measurements.

Linear sweep voltammetry (LSV)

The Gr-C-MnO₂ electrocatalyst used for the OER in the electrolyte of 0.5 M Na₂SO₄ in AcCN:H₂O (5:1) was shown to possess high electrochemical efficiency. In **Figure S8**, we conducted LSV measurements to study the formations of the reactive intermediates during the Gr-C-MnO₂-assisted OER process.



Figure S11. A LSV measurement was performed using a $Gr-C-MnO_2$ electrocatalyst in the electrolyte of 0.5 M Na₂SO₄ in AcCN:H₂O (5:1) with the scan rate of 2 mV/sec.

F. Operando Raman spectroelectrochemical investigation

In situ Raman experiments were conducted in a home-made electrochemical cell with a threeelectrode setup, containing a Ag/AgCl reference electrode, a Pt wire as a counter electrode, and the as-synthesized electrocatalyst-decorated carbon cloth as a working electrode. All reactions were performed at room temperature. The Raman scattering signal of silicon at 520 cm⁻¹ was used to calibrate the frequencies in the measured Raman spectra.

F.1. Spectral shifts of the v1, v2, and v3 bands during electrochemical reactions

In the Gr-C-MnO₂-assisted OER with 0.5 M Na₂SO₄ electrolyte, when the electrochemical potential was increased from 0 to 1 V, a substantial blue-shift of the v_1 band was observed, in contrast to the minor red-shifts of the v_2 and v_3 bands (as shown in **Figure S9a**). Since the atomic mass of Mn is ~3.5 times heavier than that of O, the motion of the O atom is mainly responsible for the Mn-O stretching vibrations (v_1 and v_2). As analyzed in Figure S4 and Figure S9b–c, the v_1 band is the out-of-plane Mn-O stretching at ~645 cm⁻¹, the v_2 bans is the in-plane Mn-O stretching at ~575 cm⁻¹, and the v₃ band is the interplanar vibration of adjacent MnO₂ nanosheets at $\sim 500 \text{ cm}^{-1}$. When the electrochemical potential was increased from 0 to 1 V, the interplanar separation of the adjacent MnO₂ nanosheets widened to allow water molecules inserting into the space between MnO₂ nanosheets and repelling Na⁺ ions (as illustrated in Figure S9c).^{S5-S6} As a result, the smaller Na⁺ ions (~2 Å in diameter) of the Na₂SO₄ electrolyte originally filled in the space between MnO₂ nanosheets could be repelled by the larger H₂O molecules (~ 2.8 Å in size). The repelled Na⁺ ions by neutral H₂O will make the highly electronegative O atom of the Mn-O bond involved in the v_1 vibration (marked by a green circle in **Figure S9b**) alienate the Na⁺ coupling, consequently increasing the vibrational frequency (i.e., causing a blue-shift) of the v_1 band. Meanwhile, the expansion of the separation between adjacent MnO_2 nanosheets (Figure S9c) slowed down the interplanar vibration of the v_3 band (i.e., making a red-shift).

In sharp contrast, the Raman signals of the D and G bands of graphene (**Figure S10**) exhibited no significant shifts in the same Gr-C-MnO₂-assisted OER in 0.5 M Na₂SO₄ electrolyte.



Figure S12. The *in situ* Raman spectra were recorded in the Gr-C-MnO₂-assisted OER with 0.5 M Na₂SO₄ electrolyte as the electrochemical potential was increased stepwise from 0.59 to 1.59 V (vs RHE). (a) The spectral shifts of Raman signals in the Mn-O vibrations (v₁: out-of-plane and v₂: in-plane) and interplanar vibration (v₃) were observed. (b) In the birnessite MnO₂ structure, the octahedral [MnO₆] moieties interconnect each other through the edge sharing to form a 2D layered structure. The v₁ band can be identified as the symmetric stretching (A_{1g}) of the Mn-O bond along the d_{z²} orbital in the octahedron of [MnO₆] (marked by a green circle). The v₂ band is attributed to the Mn-O stretching along the d_{x²-y²} orbital in the basal plane of the [MnO₆] sheet (marked by a red circle). (c) An illustration represents that the Na⁺ ions of the Na₂SO₄ electrolyte are repelled by H₂O in the interlayer space between MnO₂ nanosheets, which is widened as the applied electrochemical potential increases. The v₃ band is the interlayer vibration of adjacent MnO₂ nanosheets, which slows down as the interlayer space expands.



Figure S13. The *in situ* Raman spectra were recorded for the Gr-C-MnO₂-assisted OER in 0.5 M Na₂SO₄ electrolyte. As the electrochemical potential was increased stepwise from 0.59 to 1.59 V (vs RHE), the D and G band of graphene exhibit no significant changes.



Figure S14. The *in situ* Raman spectra were collected in the Gr-C-MnO₂-assisted OER with stepwise increment of the electrochemical potential. (a) The Gr-C-MnO₂-assisted OER was conducted in 0.5 M toluene/tetramethylammonium tetrafluoroborate electrolyte. (b) The Gr-C-MnO₂-assisted OER was performed in 0.5 M AcCN/tetramethylammonium tetrafluoroborate electrolyte.

F.2. Optimization of the Operando Raman spectroelectrochemical conditions

In the *in situ* Raman spectroelectrochemical detections of the reactive intermediates in OER, we searched the best experimental condition for the spectroelectrochemical investigation. For example, the diameter of the laser beam was maintained the same for all of the spectroscopic measurements. In the following, we varied the laser wavelength, laser power, and acquisition time to obtain the optimal conditions for subsequent experiments.

F.2.1. Selection of an excitation laser

The intensity of a Raman scattering signal depends on the wavelength (λ) of an excitation laser by λ^{-4} . Shorter laser wavelength could achieve better signal-to-noise ratios in the laser measurements.^{S4} In **Figure S12**, the intensity of the Raman scattering signal excited by 488 nm laser light is stronger than that by 633 nm. Therefore, we selected a 488 nm laser as the excitation source in the following *in situ* Raman spectroelectrochemical detections of the reactive OER intermediates in water splitting.



Figure S15. *In situ* Raman spectra of the reaction intermediates in the Gr-C-MnO₂-assisted OER performed in the electrolyte of 0.5 M Na₂SO₄ in AcCN:H₂O (5:1). The Raman spectra were observed using the excitation lasers at 488 nm and 633 nm, respectively. Stronger Raman scattering signals were obtained by applying the excitation laser at 488 nm.

F.2.2. Power of the excitation laser

With the selected excitation laser wavelength of 488 nm for the OER experiments, the intensities of Raman signals increase with increasing laser power. However, to avoid the local overheating by laser power to undermine the formation of reaction intermediates in OER, we optimized the laser power by observing the maximal Raman signals. As the laser power-dependent tests shown in **Figure S13**, the maximal Raman signals could be achieved by a 488 nm laser with the excitation power of 14 mW. Accordingly, we applied these experimental parameters in the *in situ* Raman spectroelectrochemical detections of the reactive intermediates in OER.



Figure S16. Laser power-dependent Raman scattering signals were tested in the Gr-C-MnO₂assisted OER using 0.5 M Na₂SO₄ in AcCN:H₂O (5:1) as an electrolyte. The Raman spectra were recorded with a 488 nm laser as an excitation source.

F.2.3. Exposure time of the excitation laser

The intensity of a Raman signal could be enhanced by increasing the acquisition time of the detection system used for spectral recording. However, a possible local overheating could also be created by an unnecessarily long exposure time during the signal acquisition. As examined in **Figure S14**, we varied the laser exposure time to record the spectra for detecting the reaction intermediates in the Gr-C-MnO₂-assisted OER with an electrolyte of 0.5 M Na₂SO₄ in AcCN:H₂O (5:1). Consequently, we adopted the integration time of 110 seconds for detecting the reactive intermediates in OER.



Figure S17. Laser exposure time-dependent Raman signals of the reaction intermediates were tested in the Gr-C-MnO₂-assisted OER with an electrolyte of $0.5 \text{ M} \text{ Na}_2\text{SO}_4$ in AcCN:H₂O (5:1). The experiments were conducted with a 488 nm laser of 14 mW as an excitation source.

F.3. Spectroscopic evidence of the formation of the Mn-OOH intermediate

We identified a feature at ~614.8 cm⁻¹, corresponding to the Mn-O stretching vibration of the Mn-OOH intermediate (Step D of **Figure 3b** in the main text), by careful spectral de-convolution of the observed Raman spectra taken in the Gr-C-MnO₂-assisted OER with an electrolyte of 0.5 M Na₂SO₄ in AcCN:H₂O (5:1) scanned at different potential (**Figure S15**).



Figure S18. De-convolution of the Raman spectra recorded at different potential in the Gr-C-MnO₂-assisted OER with an electrolyte of 0.5 M Na₂SO₄ in AcCN:H₂O (5:1). In the deconvolution of Raman signals, the same full width at half maximum (FWHM) was kept for all of the peaks. All the potential is in RHE scale. When the electrochemical potential was applied from 0 to 1.04 V, the vibrational signals of the v₁, v₂, and v₃ bands of birnessite MnO₂ were observed. Above 1.04 V, in addition to the v₁, v₂, and v₃ peaks, a new signal at 614.8 cm⁻¹ (marked by a blue dotted circle and represented by the blue de-convoluted peak) was observed and assigned to the Mn-O stretching vibration of the Mn-OOH intermediate.



Figure S19. (a) Using the Gr-C-MnO₂ electrocatalyst in a mixed electrolyte of 0.5 M Na₂SO₄ in AcCN:H₂O (5:1) (blue traces) or AcCN:D₂O (5:1) (red traces), the in situ Raman spectra were scanned at 300–700 cm⁻¹ (covering the Mn-O stretching region) with a stepwise increase of the electrochemical potential from 1.09 V to 1.59 V. (b) By expanding the Raman spectra in 605–630 cm⁻¹ at different potentials from 1.09 V to 1.59 V, a small red-shift of the Mn-O stretching from 614.8 cm⁻¹ (in Mn-OOH) to 613.2 cm⁻¹ (in Mn-OOD) was observed when H₂O was replaced by D₂O due to the formation of Mn-OOD.

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