Grafting Cobalt Diselenide on Defective Graphene for Enhanced Oxygen Evolution Reaction

HIGHLIGHTS
A hybrid catalyst with in-plane CoSe₂/defective graphene heterostructures

The catalyst exhibits an excellent and stable oxygen evolution reaction (OER) activity

Enhanced OER performance is due to the synergy of exposed cobalt atoms and carbon defects
Grafting Cobalt Diselenide on Defective Graphene for Enhanced Oxygen Evolution Reaction

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SUMMARY
Cobalt diselenide (CoSe2) has been demonstrated to be an efficient and economic electrocatalyst for oxygen evolution reaction (OER) both experimentally and theoretically. However, the catalytic performance of up-to-now reported CoSe2-based OER catalysts is still far below commercial expectation. Herein, we report a hybrid catalyst consisting of CoSe2 nanosheets grafted on defective graphene (DG). This catalyst exhibits a largely enhanced OER activity and robust stability in alkaline solution (overpotential at 10 mA cm⁻²: 270 mV; Tafel plots: 64 mV dec⁻¹). Both experimental evidence and density functional theory calculations reveal that the outstanding OER performance of this hybrid catalyst can be attributed to the synergetic effect of exposed cobalt atoms and carbon defects (electron transfer from CoSe2 layer to defect sites at DG). Our results suggest a promising way for the development of highly efficient and low-cost OER catalysts based on transition metal dichalcogenides.

INTRODUCTION
The oxygen evolution reaction (OER) plays an important role in various energy storage technologies, such as H₂ production from water splitting and rechargeable metal-air batteries (Hunter et al., 2016; Suen et al., 2017; Xia et al., 2016; Xu et al., 2016). However, the inherent sluggish OER kinetics, involving a four-electron transfer associated with O-H bond breaking and O-O bond formation, significantly inhibits the large-scale electrochemical water splitting (Dau et al., 2010; Suntivich et al., 2011). Although precious metal oxides (such as RuO₂ and IrO₂) have currently been employed as the state-of-the-art catalysts to overcome the drawback of very low OER kinetics, the high cost and limited resources seriously impede their widespread application (Li and Dai, 2014). As a consequence, it is crucial to explore highly efficient and inexpensive alternative catalysts that are made of geologically abundant elements.

Recently, many economical cobalt-based catalysts, including metal oxides (Masa et al., 2014), phosphates (Zhou et al., 2016), perovskite (Fabbri et al., 2013), hydro(oxy)oxides (Wan et al., 2017), and chalcogenides (Hao et al., 2017; Gao et al., 2017) have been developed and exhibited remarkable OER performance. Notably, CoSe₂, with a t₂g⁶e₅g¹ electronic configuration close to the optimal e₉ filling for OER was considered as an ideal candidate (Kong et al., 2014; Gao et al., 2012). However, the originally synthesized pure CoSe₂ catalysts still showed unsatisfied OER activity, inferior to that of the corresponding oxides or hydro(oxy)oxides. Thus, with the purpose of optimizing the OER electrocatalytic performance of CoSe₂, tremendous efforts have been made to develop diverse strategies: (1) creating strong chemical and electrical coupling by constructing hybrid structures with metals, metal oxides, or carbon materials (Zheng et al., 2015a, 2015b; Gao et al., 2014; Zhao et al., 2017a, 2017b); (2) increasing the number of active sites by reducing the thickness into atomic scale and introducing more defects (Liu et al., 2014; Liang et al., 2015); and (3) rationally engineering the electrical conductivity by doping metal cations or non-metal heteroatoms (Zhao et al., 2017a, 2017b; Fang et al., 2017). The search for new nanocomposites based on CoSe₂, which are comparable to nonprecious metal catalysts, continues (Gao et al., 2017). Specifically, modification of pure CoSe₂ by increasing its number of active sites or improving its electrical conductivity could not effectively regulate the electronic configuration of cobalt to optimize OER catalytic activity of each active site, which accordingly restrained the overall performance. To solve the problem, hybridizing with other functional materials offered a promising way. It had been demonstrated that electron-deficient cobalt with high valence could facilitate transforming O⁺ to OOH⁺ (key intermediates in OER process) (Wan et al., 2017). Therefore, if foreign materials grafted with CoSe₂ can induce electron donation from cobalt to...
the foreigners, the OER performance should be significantly promoted. However, in most previously reported hybrid OER catalysts based on CoSe2, electrons usually transferred from grafting materials to CoSe2 host, contrary to our assumption, thus encouraging us to develop new hybrid material systems for optimal performance gains.

Non-doped graphene with structural defects has recently received growing attention due to its excellent performance in electrocatalysis (Tang et al., 2016; Jia et al., 2016; Liu et al., 2017; Yan et al., 2017). Incorporation of different types of defects into the sp² structure of graphene can effectively break the integrity of π conjugation to enhance the electrocatalytic activity (Tang and Zhang, 2017). Besides, the defects on defective graphene (DG) can also offer additional efficient anchor sites for directly coupling other functional metal-based species, such as Mn-Co nanoparticles and Ni-Fe double layered hydroxide (LDH) nanosheets, through strong chemical interaction at two-phase interface (Yan et al., 2016; Jia et al., 2017). These hybrid catalysts can exhibit much better electrochemical performance than individual components due to their unique structural features such as highly exposed active sites on 2D nanolayers, conductive graphene substrates, as well as enhanced proton coupling and electron transport between the components. Particularly, in the case of Ni-Fe LDH nanosheets hybridized with DG, density functional theory (DFT) calculations had confirmed the accumulation of holes on Ni-Fe LDH nanosheets and that of electrons at the defect sites in DG (Jia et al., 2017). In this regard, properly integrating pre-synthesized 2D conductive graphene substrates, as well as enhanced proton coupling and electron transport between the components. Particularly, in the case of Ni-Fe LDH nanosheets hybridized with DG, density functional theory (DFT) calculations had confirmed the accumulation of holes on Ni-Fe LDH nanosheets and that of electrons at the defect sites in DG (Jia et al., 2017). In this regard, properly integrating pre-synthesized 2D CoSe2@DG nanosheets onto DG may be an effective way to modulate the interfaces and chemical and electronic structures to access optimized OER energetics.

Herein, we report that exfoliated ultrathin CoSe2 nanosheets can be grafted with DG to form a CoSe2@DG hybrid OER catalyst by a facile hydrothermal method. Benefiting from the synergistic effect between CoSe2 and DG substrate, the as-prepared CoSe2@DG nanocomposite exhibits a remarkable performance toward OER. The OER overpotential at a current density of 10 mA cm⁻² is only 270 mV and a high current density of 129 mA cm⁻² is obtained at an overpotential of 350 mV, which can be ranked as the top-performing one among the hitherto reported CoSe2-based OER catalysts. In addition, the CoSe2@DG electrode also demonstrates an outstanding stability after a long-term cycle measurement. This work demonstrated that the CoSe2@DG will be a very promising nonprecious metal-based OER catalyst.

RESULTS
Synthesis and Characterization of CoSe2@DG Composite Catalysts
As illustrated in Figure 1A, the whole synthesizing process includes two steps: (1) ultrasound induced liquid exfoliation of pre-synthesized lamellar CoSe2/DETA (diethylenetriamine) intermediate (Liu et al., 2014) and (2) assembling ultrathin CoSe2 nanosheets with DG via a simple hydrothermal route. For the first step, a homogeneously dispersed black suspension was obtained after the ultrasonic exfoliation process, which could keep stable for a long time without any precipitate (Figure 1A, inset). Morphology characterization (scanning electron micrographs and transmission electron microscopic images in Figures S1 and S2) clearly confirmed the formation of ultrathin CoSe2 nanosheets (denoted as E-CoSe2). X-ray diffraction (XRD) patterns showed weaker characteristic peaks when compared with pristine CoSe2/DETA, which further demonstrated the well-done exfoliation (Figure 1G, red). The thickness of the exfoliated nanosheets was measured to be around 3 nm from the atomic force microscopic image, corresponding to about 5 layers (a single CoSe2 layer along the lattice parameter is ~0.61 nm) (Gao et al., 2009). Subsequently, these CoSe2 ultrathin sheets could be tightly overlain on the DG in a certain mass ratio (typically 9:1) by a hydrothermal treatment process at 60°C for 24 hr. TEM images revealed that the smooth and near-transparent surface of DG sheets became extremely rougher and opaque, indicating the successful grafting of CoSe2 onto DG (Figures 1C and 1D). The high-resolution TEM image in Figure 1E showed the lattice fringe with a spacing of 2.67 Å, which can be assigned to the (210) plane of cubic-phase CoSe2. The interlayer distance could be estimated to be ~5.5 Å, smaller than that of pristine CoSe2/DETA, which was attributed to the removal of DETA molecules during the exfoliation process (Figure 1F). Further experiments revealed that the mass ratio of CoSe2/DG showed a considerable influence on the morphology of the products (Figure S3). When decreasing the mass ratio to 3:1 or 6:1, only partially and non-uniformly covered CoSe2@DG hybrids could be obtained. In addition, DG support also plays an important role in the synthesis. To demonstrate it, CoSe2@G (G presents pristine graphene) and CoSe2@NG (NG represents nitrogen-doped G) samples were fabricated for comparison using the same method. As illustrated in the TEM images, aggregated CoSe2 only anchored on part of G or NG sheet surface, in contrast to the entirely covered morphology for CoSe2@DG (Figure S4). This indicates that DG is more suitable as the support for CoSe2 nanosheet
dispersion and anchoring, effectively preventing the aggregation of CoSe₂ nanosheets, which should be beneficial for the catalytic performance enhancement.

To further investigate the microstructure and composition of as-prepared CoSe₂@DG composites, a series of measurements were carried out. XRD pattern of CoSe₂@DG nanocomposites still exhibited the featured diffraction peaks of CoSe₂, suggesting that no phase change occurred during the synthesis process (Figure 1G, blue). The intensity of all the peaks was a bit stronger than that of exfoliated ultrathin CoSe₂ nanosheets, but still much weaker than that of original CoSe₂/DETA, indicating only a small part of ultrathin nanosheets reassembled. In addition, the energy-dispersive X-ray spectrum and elemental mapping indicated the existence of elements C, Co, Se and their uniform distribution in the hybrids, also confirming the formation of CoSe₂@DG composites (Figures 1H and S5). The Co loading amount in as-made CoSe₂@DG,
CoSe$_2$@DG, and CoSe$_2$@NG composites was obtained according to the thermogravimetric analysis as 31.6, 28.9, 29.5 wt%, respectively (Figure S6). Based on this, we further calculated the number of moles ($n$) of Co element in different catalysts deposited on the glass carbon electrode (CoSe$_2$@DG: 0.132 mol; CoSe$_2$@G: 0.121 mol; CoSe$_2$@NG: 0.124 mol), which could be used to gain the turnover frequency (TOF) value for the evaluation of their intrinsic OER efficiency.

**OER Performance of CoSe$_2$@DG Catalysts-Coated Glass Carbon Electrode**

Using a standard three-electrode system, the electrocatalytic OER properties of different samples were evaluated in an O$_2$-saturated 1 M KOH aqueous solution ($4\text{OH}^- + \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$. The as-prepared catalysts were uniformly cast on a glassy carbon electrode with a loading of 0.2 mg cm$^{-2}$ and used as a working electrode. The OER activities of CoSe$_2$@DG composites prepared with different mass ratios (3:1, 6:1, and 9:1) were first studied to determine the optimal synthetic condition. As shown in Figure S7, CoSe$_2$@DG-9-1 exhibited the best OER activity among the three products, with the smallest overpotential at 10 mA cm$^{-2}$, the largest current density at an overpotential of 0.35 V, and the fastest kinetics. The results should be attributed to their morphological difference mentioned above. Reassembly of CoSe$_2$ nanosheets in CoSe$_2$@DG-3-1 and CoSe$_2$@DG-6-1 samples significantly inhibited their OER performance. If not specially specified, the CoSe$_2$@DG, CoSe$_2$@NG, and CoSe$_2$@G products are all synthesized in the mass ratio of 9:1 in this research. Subsequently, the OER activities for other comparative samples, such as CoSe$_2$ nanosheets coupling with different graphene (NG, G), exfoliated CoSe$_2$ nanosheet (E-CoSe$_2$), CoSe$_2$ nanosheets physically mixed with DG (CoSe$_2$/DG), and the OER benchmark catalyst (RuO$_2$), were also measured. Figure 2A shows polarization curves recorded by linear sweep voltammetry (LSV) at a slow scan rate of 5 mV s$^{-1}$ with a continuous rotating speed of 1,600 rpm after internal resistance ($iR$) correction. Among the five tested catalysts, CoSe$_2$@DG displayed the highest intrinsic OER activity. To reach a current density of 10 mA cm$^{-2}$, CoSe$_2$@DG required an overpotential of only 270 mV, which was 35, 22, 20, 106, and 83 mV smaller than that

![Figure 2. OER Performance of CoSe$_2$@DG Composite Catalysts](image-url)
of commercial RuO$_2$, E-CoSe$_2$, CoSe$_2$/DG mixture, CoSe$_2$@G, and CoSe$_2$@NG, respectively (Figure 2B). The current density at an overpotential of 350 mV was 129 mA cm$^{-2}$, which was 6, 2.1, 2, 23.7, and 16.5 times higher than that of RuO$_2$, E-CoSe$_2$, CoSe$_2$/DG mixture, CoSe$_2$@G, and CoSe$_2$@NG, respectively (Figure 2C). Meanwhile, the intrinsic activity of different catalysts was assessed by TOF, assuming all the Co element was catalytically active (Figure S8). Compared with RuO$_2$, E-CoSe$_2$, CoSe$_2$@G, and CoSe$_2$@NG catalysts, the CoSe$_2$@DG hybrids exhibited obviously larger TOF value of 0.024 s$^{-1}$ at an overpotential of 270 mV, indicating the significant role of interaction between CoSe$_2$ and DG toward OER in our study. As all the active sites were presumed to come from CoSe$_2$, comparative experiment was also offered to confirm that DG was inert in OER relative to CoSe$_2$ (Figure S9). Furthermore, the kinetic parameters of OER for the five catalysts were also calculated (Figure 2D). CoSe$_2$@DG had a Tafel slope of about 64 mV dec$^{-1}$, similar to that of E-CoSe$_2$ (66 mV dec$^{-1}$), CoSe$_2$/DG mixture (66 mV dec$^{-1}$), and RuO$_2$ (69 mV dec$^{-1}$), but much smaller than that of the other samples (83 mV dec$^{-1}$ for CoSe$_2$@NG and 92 mV dec$^{-1}$ for CoSe$_2$@G). The above OER measurement was done in 1 M KOH solution. However, in some cases, OER catalysts were reported to assess their activity in 0.1 M KOH solution (Liu et al., 2014). Therefore, to achieve a more accurate comparison of the OER performance between our synthesized CoSe$_2$@DG hybrid catalyst and other nonprecious metal catalysts, we also measured its OER LSV curves in 0.1 M KOH solution and found that it only required an overpotential of 304 mV to afford a current density of 10 mA cm$^{-2}$ (Figure S10). In fact, the activity of CoSe$_2$@DG has outperformed those of most CoSe$_2$-based OER catalysts reported to date and is comparable to those of other state-of-the-art nonprecious metal catalysts (Table S1). To gain further insight of the OER kinetics occurring on such CoSe$_2$@DG hybrid catalysts, electrical impedance spectroscopy was performed. The CoSe$_2$@DG composites exhibited a much smaller charge transfer resistance of 42 Ω than that of E-CoSe$_2$ of 88 Ω (Figure S11). Moreover, the double layer capacitance ($C_{dl}$) was obtained through the cyclic voltammetry measurement, which was considered as an alternative method to estimate the electrochemical active surface areas (ECSAs) (Figures 2E and S12). The CoSe$_2$@DG composites show a $C_{dl}$ of 28.1 mF cm$^{-2}$, much larger than that of E-CoSe$_2$ nanosheets (9.3 mF cm$^{-2}$), indicating that the effective combination of CoSe$_2$ and DG leads to an increased ECSA and more exposed active sites.

To assess the stability of the conditioned CoSe$_2$@DG electrode, the continuous amperometric i-t measurement was employed under a constant overpotential of 305 mV. Figure 2F displayed that the current density maintained at ~ 31 mA cm$^{-2}$ during 10 hr and the polarization curve after i-t measurement showed negligible current loss, demonstrating the high electrocatalytic durability of CoSe$_2$@DG. Various postmortem characterizations reveal no obvious change in the structure of CoSe$_2$@DG catalysts after OER stability test, further evidencing their remarkable catalytic robustness in alkaline medium (Figure S13).

Catalytic Mechanism by Synergistic Effect of CoSe$_2$ with DG

It is imperative to gain a comprehensive understanding of the intrinsic reason for the improved OER performance after the effective coupling of CoSe$_2$ and DG. To achieve this goal, both experimental and theoretical methods were used. First, the strong interactions between CoSe$_2$ and DG in the composites were demonstrated experimentally by Raman scattering and X-ray photoelectron spectroscopic (XPS) measurements, indicating that the synthetic effect should play a vital role for OER enhancement (Figure 3).
As shown in Figure 3A, both E-CoSe₂ and CoSe₂@DG samples exhibited four characteristic peaks corresponding to the cubic CoSe₂ (Campos et al., 2002). Notably, the Raman peak at ~660 cm⁻¹ shifted to lower wave number after incorporating CoSe₂ with DG, suggesting the charge transfer between CoSe₂ nanosheets and DG substrates, which resembled previous observation in the case of CoO₂/CoSe₂ and Au cluster/CoSe₂ composites (Zheng et al., 2015a, 2015b; Zhao et al., 2017a, 2017b). In addition, we also compared the Raman spectra of DG and CoSe₂@DG and found that the characteristic D band (1,344 cm⁻¹) and G band (1,574 cm⁻¹) became much weaker after anchoring CoSe₂ on DG (Figure S14) (Banhart et al., 2011). This change can be ascribed to the relatively low amount of DG in the CoSe₂@DG composite (prepared in the mass ratio of 9:1 for CoSe₂ and DG as depicted above). To further confirm the interaction between CoSe₂ layer and defects on DG, XPS of E-CoSe₂ and CoSe₂@DG were carried out. The Co³⁺ cations were generally believed to be the real reason for the decent OER activity, which could facilitate the formation of O−OH (key intermediates in OER) and then further be oxidized to produce O₂ (Chen et al., 2016; Yeo and Bell, 2011). As shown in the high-resolution Co 2p spectra, there existed obvious characteristic peaks of Co²⁺ and Co³⁺ cations, which was in accordance with that of CoSe₂ materials reported previously (Figure 3B) (Li et al., 2017). Of note, the electron binding energy of Co 2p in CoSe₂@DG composites showed an ~0.4 eV increase compared with pure E-CoSe₂, which indicated the effective electron transfer from CoSe₂ to DG (Gao et al., 2012; Zheng et al., 2015a, 2015b). Both Raman spectra and XPS results demonstrated that the synergetic effect between CoSe₂ and DG could change the electron configuration in the composites, which consequently promoted their OER performance. Moreover, perhaps someone will wonder whether the hydrothermal process has positive influence on the CoSe₂ layers for the improved OER activity of final CoSe₂@DG composites. To exclude it, hydrothermal-treated CoSe₂ (H-CoSe₂) without DG was also prepared (Figure S15). LSV curves illustrated that H-CoSe₂ showed decreased OER activity than original E-CoSe₂, further proving that the synergetic effect of CoSe₂ and DG was the cause of the enhanced OER performance for CoSe₂@DG composites.

Based on above experimental data, we have attributed the enhanced OER activity after coupling CoSe₂ nanosheets and DG to the effective charge transfer from CoSe₂ layer to DG. To further demonstrate it, we conducted a series of DFT calculations (see computational details in the Supplemental Information). In a previous study, we have confirmed that different defect types (denoted as DG-5, DG-585, and DG-5775 defect) on DG serve as highly efficient catalytically active sites (Jia et al., 2016). Therefore, we chose the three defect types as the computational models of DG in this part. Figures 4A–4C and S16 showed the geometries of the fully relaxed CoSe₂@DG-5, CoSe₂@DG-585, CoSe₂@DG-5775, CoSe₂@NG, and CoSe₂@G composites in side view and their charge density differences. It could be seen clearly that the electrons were inclined to redistribute around the 5 and 585 defect sites, resulting in the charge depletion on CoSe₂ layer, which favors OER (Figure 4D). In contrast, the electron transfer in the other three models was negligible. The calculation results on the charge transfer between the two components were consistent with our experimental data. Moreover, we also calculated the Gibbs free energy differences for OER occurring on CoSe₂@DG, CoSe₂@NG, CoSe₂@G composites, and pristine CoSe₂ (Figure 4E). The ideal barrier (1.23 eV) for each step was also included for comparison (black thick line). The overpotential was determined by the largest Gibbs free energy barrier. For the pristine CoSe₂, CoSe₂@G, CoSe₂@DG, and CoSe₂@NG composites, the third step (O* is transformed to OOH*) is the rate-determining step. As observed, the CoSe₂@DG composite possessed the lowest Gibbs free energy with a barrier of 1.39 eV among the models, indicating its best OER activity. Both experimental and theoretical results demonstrate that the charge depletion on CoSe₂ induced by the electron transfer from CoSe₂ to DG is the cause of the outstanding OER performance of the CoSe₂@DG catalysts.

DISCUSSION

In summary, we have successfully grafted exfoliated CoSe₂ nanosheets onto the DG to prepare a new CoSe₂@DG composite by a hydrothermal process. The hybrid catalyst displays excellent OER performance with a small overpotential of ~270 mV at a current density of 10 mA cm⁻², large anodic current density of ~129 mA cm⁻² at an overpotential of 350 mV, and good durability in alkaline solution, which is superior to most reported CoSe₂-based OER catalysts. Based on our experimental analysis and DFT calculations, the improved OER activity can be attributed to the synergistic effect (charge redistribution) between CoSe₂ nanosheets and DG substrates. This work will raise promising possibilities for designing advanced OER electrocatalysts via synergistically coupling nonprecious metal-based materials with DG, which is highly desirable for energy conversion technologies.
Limitations of Study

This work proposes a promising avenue to enhance catalytic performance by effective hybridization of carbon defects and foreign materials. Although demonstrated theoretically, the fabrication of a certain type of carbon defect is now experimentally unavailable, limiting the further optimization of catalytic energetics for such composite catalysts.

METHODS

All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION

Supplemental Information includes Transparent Methods, 16 figures, and 1 table and can be found with this article online at https://doi.org/10.1016/j.isci.2018.08.013.

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AUTHOR CONTRIBUTIONS
X.W. and L.Zhuang contributed equally to this work. X.W., L.Zhuang, X.Yao, and S.Y. conceived and designed the experiments. M.G., Z.Z., X.Yao, and S.H.Y. supervised the project. X.W., L.Zhuang, Y.J., L.Zhang, and X.Yan performed the synthesis experiments, material characterization, and OER measurement. T.H. and A.D. performed the DFT calculation. All authors discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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Supplemental Information

Grafting Cobalt Diselenide on Defective Graphene for Enhanced Oxygen Evolution Reaction

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Supplemental Information

Supplemental Figures

Figure S1. Characterization of CoSe$_2$/DETA hybrids, related to Figure 1.
SEM (A) and TEM (B) images of synthesized CoSe$_2$/DETA hybrids.

Figure S2. Characterization of exfoliated CoSe$_2$ ultrathin nanosheets, related to Figure 1.
TEM images of exfoliated CoSe$_2$ ultrathin nanosheets.
Figure S3. Characterization of different CoSe$_2$@DG samples, related to Figure 1.
TEM images of CoSe$_2$@DG samples prepared with the mass ratio of CoSe$_2$/DG as (A) 3:1 and (B) 6:1.

Figure S4. Characterization of CoSe$_2$@G and CoSe$_2$@NG composites, related to Figure 1.
STEM-EDS elemental mapping images of (A) CoSe$_2$@G and (B) CoSe$_2$@NG composites.
Figure S5. Characterization of CoSe$_2$@DG composites, related to Figure 1.
EDX spectrum of as-prepared CoSe$_2$@DG composites.
Figure S6. Characterization of CoSe$_2$@G, CoSe$_2$@NG, and CoSe$_2$@DG composites, related to Figure 1.
TGA curve of (A) CoSe$_2$@DG (B) CoSe$_2$@G (C) CoSe$_2$@NG composites under air atmosphere.

Figure S7. OER activity of CoSe$_2$@DG composites prepared with different mass ratio (3:1, 6:1, and 9:1), related to Figure 2.
(A) LSV curves, (B) Tafel plots, (C) Overpotential required for $j=10$ mA cm$^{-2}$, (D) Current densities at an overpotential of 350 mV.
Figure S8. Intrinsic activity study of different catalysts, related to Figure 2.
Turnover frequency (TOF) of different catalysts at an overpotential of 270 mV.

Figure S9. Comparison of OER activity between DG and CoSe$_2$@DG hybrid, related to Figure 2.
OER LSV curves of DG and CoSe$_2$@DG hybrid in 1 M KOH solution.
Figure S10. OER activity of CoSe$_2$@DG hybrid catalysts in 0.1 M KOH solution, related to Figure 2. OER LSV curve of CoSe$_2$@DG hybrid catalysts in 0.1 M KOH solution.

Figure S11. Impedance study of E-CoSe$_2$ and CoSe$_2$@DG related to Figure 2. Electrochemical impedance spectroscopy (EIS) Nyquist plots obtained at 1.33 V vs. RHE.
Figure S12. The electrochemical active surface areas (ECSAs) study of E-CoSe$_2$ and CoSe$_2$@DG catalysts, related to Figure 2.

Cyclic voltammetry curves of (A) E-CoSe$_2$ and (B) CoSe$_2$@DG catalysts at different scanning rate.

Figure S13. Characterization of CoSe$_2$@DG catalysts after continuous amperometric i-t measurement, related to Figure 2.

(A) TEM image, Inset: HRTEM image, (B) XRD patterns, (C) Co 2p XPS spectra, and (D) EDX spectrum.
Figure S14. The study on the interaction between CoSe$_2$ and DG support, related to Figure 3. 
Raman spectra of pure DG and as-prepared CoSe$_2@DG$ composites.

Figure S15. Characterization and OER activity of hydrothermal treated CoSe$_2$ (H-CoSe$_2$) without DG, related to Figure 3.
(A) TEM image of H-CoSe$_2$; (B) OER LSV curves of E-CoSe$_2$ and H-CoSe$_2$ samples.
**Figure S16.** Charge density distribution of CoSe$_2$@NG and CoSe$_2$@G related to Figure 4.
The side views of 3D charge density difference plot for the interfaces between graphene sheets (A for NG and B for G) and CoSe$_2$ layer calculated by DFT. Yellow and cyan isosurfaces represent charge accumulation and depletion in the 3D space with an isosurface value of 0.002 e Å$^{-3}$. Brown, green and blue balls represent C, Se and Co atoms, respectively.

**Supplemental Table**

**Table S1.** Electrocatalytic OER performance of our synthesized CoSe$_2$@DG hybrid catalysts compared with that of reported other non-precious metal electrocatalysts tested in alkaline solution, related to Figure 2.

| Material                  | Electrolyte | $\eta$@10 mA cm$^{-2}$ (mV) | $j$@350 mA cm$^{-2}$ (mA cm$^{-2}$) | Tafel slope (mV dec$^{-1}$) | Reference |
|---------------------------|-------------|------------------------------|------------------------------------|----------------------------|-----------|
| CoSe$_2$@DG               | 1M KOH      | 270                          | 129                                | 64                         | This work |
|                           | 0.1M KOH    | 304                          | >20                                | N/A                        |           |
| CoSe$_2$ ultrathin nanosheets | 0.1M KOH    | 320                          | <20                                | 44                         | (Liu et al., 2014) |
| Metallic single-unit-cell CoSe$_2$ sheets | 1M KOH    | ~340                          | <15                                | 64                         | (Liang et al., 2015) |
| CoSe$_2$/CF                | 1M KOH      | 297                          | <50                                | 41                         | (Sun et al., 2016) |
| CoSe$_2$/N-graphene        | 0.1M KOH    | 366                          | <10                                | 40                         | (Gao et al., 2014) |
| CeO$_2$/CoSe$_2$           | 0.1M KOH    | 288                          | N/A                                | 44                         | (Zheng et al., 2015) |
| Composition                          | KOH Concentration | Time (min) | Current Efficiency (%) | Capacity (mAh g\(^{-1}\)) | Reference               |
|-------------------------------------|-------------------|------------|------------------------|----------------------------|-------------------------|
| Au nanoclusters/CoSe\(_2\)          | 0.1M KOH          | 410        | <5                     | N/A                        | (Zhao et al., 2017)     |
| Ag-CoSe\(_2\)                       | 0.1M KOH          | 320        | 22.36                  | 56                         | (Zhao et al., 2017)     |
| NiSe\(_2\) nanosheets               | 1M KOH            | 330        | 16.3                   | 80                         | (Chen et al., 2017)     |
| (Ni,Co)Se\(_2\)-GA                  | 1M KOH            | 250        | >100                   | 70                         | (Xu et al., 2017)       |
| CoTe\(_2\)                          | 0.1M KOH          | 357        | <20                    | 32                         | (Gao et al., 2017)      |
| N-doped CoS\(_2\)                   | 1M KOH            | 240        | ~150                   | 98                         | (Hao et al., 2017)      |
| Fe-CoOOH/G                           | 1M KOH            | 330        | ~30                    | 37                         | (Han et al., 2017)      |
| CoFe LDHs-Ar                         | 1M KOH            | 266        | N/A                    | 37.85                      | (Wang et al., 2017)     |

**Transparent Methods**

**Synthesis of CoSe\(_2\)-DETA lamellar nanohybrids**

In a typical procedure, 2 mmol (0.498 g) of Co(Ac)\(_2\)⋅H\(_2\)O was added into 26.0 mL of deionized water (DIW) under magnetic stirring. About 10 min later, 2 mmol (0.346 g) of Na\(_2\)SeO\(_3\) and 52.0 mL of diethylenetriamine (DETA) were added. After stirring for 0.5 h in a beaker, the wine homogeneous solution was transferred into a 100 mL Teflon-lined autoclave, which was sealed and maintained at 180 °C for 16 h and then naturally cooled down to room temperature. The resulting solid product was collected and washed with absolute ethanol for 3 times to remove ions and possible remnants, and dried under vacuum at 60 °C for 16 h.

**Exfoliation of CoSe\(_2\)-DETA lamellar nanohybrids**

20 mg of CoSe\(_2\)-DETA product was dispersed in 40 mL of ethanol and then ultrasonicated in ice-water for 12 h. After ultrasonic treatment, the resultant dispersions were centrifuged at 9500 rpm for 10 min to remove the unexfoliated component. The supernatant is denoted as the exfoliated CoSe\(_2\) nanosheet (E-CoSe\(_2\)) solution.

**Synthesis of N doped graphene (NG) and defective graphene (DG)**

Typically, the monolayer pristine graphene was mixed with melamine (mass ratio was 1:1), and annealed at 700 °C for 2 hours with a heating rate of 5 °C min\(^{-1}\) under nitrogen to prepare the NG. Before heating, two hours nitrogen gas flowing was needed to remove oxygen in the furnace tube. Then to prepare DG, NG was annealed at 1150 °C for 2 hours with a heating rate of 5 °C/min under nitrogen so as to subtract the nitrogen atom from the sample.

**Synthesis of the CoSe\(_2\)@DG composite**

Typically, a designed volume of DG NG or G nanosheet (0.1 g L\(^{-1}\)) was added drop by drop into the exfoliated CoSe\(_2\)-NS solution under continuous stirring (the mass ratio of exfoliated CoSe\(_2\) ultrathin
The solution was transferred into a 100 mL Teflon-lined autoclave, sealed and maintained at 60 °C for 12 h, and then naturally cooled to room temperature. The resulting product was separated by centrifugation.

Materials characterization

The samples were characterized by different analytic techniques. X-ray diffraction (XRD) patterns (2θ, 8-90°) were recorded on a Bruker D8-Advanced X-ray diffractometer using nickel-filtered Cu-Kα radiation. Electron microscope images were collected on a JEOL JSM-7001F scanning electron microscopy (SEM) at an acceleration voltage of 10 kV and a Tecnai 20 FEG transmission electron microscope (TEM) operated at 200 kV. X-ray photoelectron spectra were acquired on a Kratos Axis ULTRA X-ray photoelectron spectrometer (XPS) incorporating a 165 mm hemispherical electron energy analyser and a monochromatic Al Kα (1486.6 eV) radiation at 150 W (15 kV, 10 mA). The binding energies were determined using the C1s line at 284.6 eV from adventitious carbon as a reference. Raman spectra were recorded on a Renishaw InVia spectrometer using the 514 nm laser excitation. Thermogravimetric analysis (TGA) was carried out on a TA Instrument under air at a heating rate of 10 °C min⁻¹. The thickness of CoSe₂-NS was analysed by a Cypher (Asylum Research) atomic force microscope (AFM), whose cantilevers were HA_NC (Etalon) from NT-MDT, having a nominal spring constant of 4.5 N/m and nominal resonant frequency of 145 kHz.

Electrochemical measurements

All the electrochemical tests were performed in a conventional three-electrode system at an electrochemical station (Biologic VMP2/Z multichannel potentiostat), using Pt wire as counter electrode, glassy carbon electrode as working electrode, and an Ag/AgCl (3 M NaCl) electrode as reference electrode. For the preparation of CoSe₂ thin film electrode, 5 mg of catalyst powder was dispersed in 1 mL of 3:1 (v/v) DIW/2-propanol mixed solvent with 40 μL of Nafion solution (5 wt%), and then the mixture was ultrasonicated for about 1 h to generate a homogeneous ink. Next, 5.0 μL of the dispersion was transferred onto the glassy carbon disk, leading to the catalyst loading of 0.196 mg cm⁻². Finally, the as-prepared catalyst film was dried at room temperature. Linear sweep voltammetry (LSV) was performed at a continuous rotating speed of 1,600 rpm and a sweep rate of 5 mV/s. To assess the long-term electrocatalytic stability of CoSe₂@DG electrodes, the continuous amperometric i-t measurement was employed under a constant overpotential of 305 mV. The electrochemical impedance spectroscopy (EIS) measurement was carried out in the same configuration at room temperature with a sinusoidal voltage amplitude of 10 mV. The electrochemically active surface areas (ECSA) was determined by CV at the potential window 0.987 – 1.087 V (vs. RHE), with different scanning rate of 10, 20, 30, 40, and 50 mV/s. By plotting the difference between the anodic and cathodic current densities (Δj= ja - jc) at 1.037 V (vs. RHE) against the scan rates, the resulting linear slope is twice of the double layer capacitance (Cdl), which can be used to represent ECSA. The turnover frequency (TOF) value is calculated according to the following equation:

\[
\text{TOF} = \frac{(J \times A)}{(4 \times F \times n)}
\]

where J is the current density at a given overpotential (270 mV for our work), A is the surface area of the electrode (0.126 cm²), the number of 4 represents 4 electrons/mol of O₂, F is the Faraday constant (96485.3 C/mol), and n stands for the number of moles of Co ions in as-made CoSe₂@DG, CoSe₂@G, CoSe₂@NG composites. In our case, all Co element was assumed to be catalytically active no matter whether they are...
accessible to the electrolyte or not. Therefore, the calculated TOF value represents the lowest limit.

RHE calibration: In the all electrochemical tests, Ag/AgCl (3M NaCl) was used as the reference electrode. It was calibrated with regard to RHE. The calibration was performed in a H₂-saturated 1 M KOH electrolytes with a Pt-wire as the working electrode. CV curve was obtained at the scan rate of 1 mV s⁻¹, and the average potential at which the current crossed zero was regard as the thermodynamic potential for the hydrogen electrode reaction. The CV curve was shown as below:

\[
\begin{array}{c}
\text{Hydrogen oxidation} \\
1.0 \text{ M KOH} \\
1.024 \text{ V} \\
\text{Hydrogen evolution}
\end{array}
\]

In 1 M KOH solution, all potentials were referenced to reversible hydrogen electrode (RHE) by following calculations: \( E(\text{RHE}) = E(\text{Ag/AgCl}) + 1.024 \text{ V} \).

Computational details

Density functional theory (DFT) as implemented in the Vienna Ab-initio Simulation Package (VASP) code were employed to perform the calculations (Kresse and Furthmüller, 1996a, 1996b). We use the generalized gradient approximation (Perdew et al., 1996) in the form of the Perdew–Burke–Ernzerhof functional (Perdew et al., 1996) to describe exchange-correlation interactions. Blöchl’s all-electron, frozen-core projector augmented wave (PAW) method (Blöchl, 1994) was used to represent nuclei and core electrons. In all calculations, the van der Waals interaction was described by using the empirical correction in Grimme’s scheme, i.e., DFT+D3 (Grimme, 2006). The Brillouin zone is sampled by gamma point. The electron wave functions were expanded using the plane waves with a cut off energy of 500 eV.

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