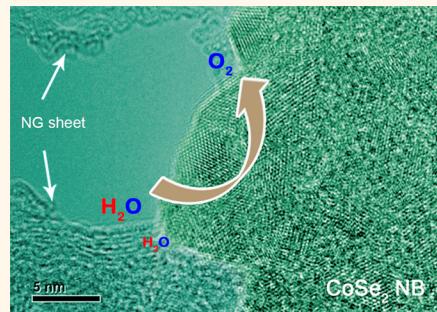


Nitrogen-Doped Graphene Supported CoSe₂ Nanobelt Composite Catalyst for Efficient Water Oxidation

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ABSTRACT The slow kinetics of the oxygen evolution reaction (OER) greatly hinders the large-scale production of hydrogen fuel from water splitting. Although many OER electrocatalysts have been developed to negotiate this difficult reaction, substantial progresses in the design of cheap, robust, and efficient catalysts are still required and have been considered a huge challenge. Here, we report a composite material consisting of CoSe₂ nanobelts anchored on nitrogen-doped reduced graphene oxides (denoted as NG-CoSe₂) as a highly efficient OER electrocatalyst. In 0.1 M KOH, the new NG-CoSe₂ catalyst afforded a current density of 10 mA cm⁻² at a small overpotential of mere 0.366 V and a small Tafel slope of ~40 mV/decade, comparing favorably with the state-of-the-art RuO₂ catalyst. This NG-CoSe₂ catalyst also presents better stability than that of RuO₂ under harsh OER cycling conditions. Such good OER performance is comparable to the best literature results and the synergistic effect was found to boost the OER performance. These results raise the possibility for the development of effective and robust OER electrodes by using cheap and easily prepared NG-CoSe₂ to replace the expensive commercial catalysts such as RuO₂ and IrO₂.



KEYWORDS: nitrogen-doped graphene · composite catalysts · water oxidation · cobalt selenides · nanobelts

Conversion of electricity captured from the sustainable but intermittent energy sources (e.g., wind and sunlight) into H₂ fuel by the electrochemical splitting of water is considered one of the holy grails of chemistry.^{1,2} However, the oxygen evolution reaction (OER) at the anode suffers from a complex four-electron oxidation process and sluggish kinetics, which imposes considerable electrochemical overpotential (η) requirements that lead to significant losses to the overall efficiency of water splitting.^{3–5} Catalyst development is critical to address this challenge. Current commercial water electrolyzers still rely on the use of ruthenium (Ru) and iridium (Ir) oxides as OER catalysts although their limited availability and high cost.^{6,7} As a consequence, the discovery of robust and efficient alternative catalysts that are geologically abundant is highly needed to viable water electrolytic systems.

In recent years, cobalt (Co) has become one of the most popular non-noble metals for the design of robust OER catalysts, including simple^{8–13} and mixed-metal oxides,^{14–16}

hydro(oxy)oxides,¹⁷ phosphates,^{18–23} chalcogenides,^{24,25} perovskites,^{3,26} and molecular catalysts.^{27,28} Besides abundance and low cost, these Co compounds are advantageous for affording water oxidation with moderate overpotentials under neutral or alkaline conditions. More promisingly, numerous studies have shown that, after incorporating other functional materials, the OER performance of the single Co compounds can be greatly optimized.^{8,9,13,17,23–25} For example, Gamelin *et al.* reported the intergration of “Co-Pi” OER catalyst with α -Fe₂O₃ can substantially reduce the external power for catalyst's electrolysis chemistry,²³ and the intrinsic reasons for such improvement were proposed by Barroso and co-workers.²⁹ Jiao and Frei,⁸ Yeo and Bell,⁹ and Dai *et al.*¹³ have developed several remarkable Co₃O₄-based OER catalysts by anchoring them on mesoporous silica scaffolds, Au supports, and graphene sheets, respectively.

We recently made big efforts to design efficient electrocatalysts^{24,30–33} based on a new lamellar mesostructured CoSe₂/DETA (DETA = diethylenetriamine) nanobelts³⁴

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and observed much enhanced OER activity and stability in alkaline solution after modifying them with Mn_3O_4 nanoparticles.²⁴ The synergistic chemical coupling effects between Co compounds and introduced materials was believed to contribute the substantial enhancement. Despite great successes, very few such Co-based catalysts were found to be comparable to or exceed the expensive commercial RuO_2 and IrO_2 catalysts.³

Graphene sheets (2010 Nobel Physics Prize), are becoming an inexpensive material, have been proven an outstanding matrix to support foreign materials, leading to advanced materials for electrocatalysis and other energy-related applications.^{35–38} Considering that, after growing foreign materials onto graphene, the strong chemical and electrical coupling, as well as the possibly optimized electronic structure, can bring significant performance gains,³⁸ we report here a rationally designed Co-based composite catalyst, *i.e.*, nitrogen-doped reduced graphene/CoSe₂ nanobelts (denoted as NG-CoSe₂ nanobelts), exhibits high OER electrocatalytic performance with low η and small Tafel slope, even comparing favorably with the commercial RuO_2 catalyst in alkaline medium.

RESULTS AND DISCUSSION

We selected graphene as substrate by taking advantage of its high electrical conductivity, large surface area, high chemical stability, and mechanical

strength.³⁸ Through a simple hydrothermal reduction method, ultralong CoSe₂ nanobelts with thin and flexible features could be tightly overlain the graphene sheets (Figure 1 and Supporting Information Figure S1). Such combination can afford the composite catalyst (1) a largely exposed CoSe₂ surfaces as OER active substance in that they are nailed down by NG, preventing undesired aggregates, (2) a high electrical conductivity based on the intimate connection between CoSe₂ nanobelts and NG, and (3) an optimal chemical coupling between the two materials. These merits together endue the NG-CoSe₂ catalyst exceptional OER performance in alkaline solution although pure CoSe₂ only shows small activity and NG is almost OER inactive.

First, large graphene oxide (GO) sheets (Supporting Information, Figure S2) were prepared by oxidation of graphite flakes (Sigma-Aldrich) through the Hummers method,³⁹ which were then used as supports to provide places for the nucleation and growth of CoSe₂ nanobelts in a closed DETA/H₂O hydrothermal system (Figure 1a, also see Experimental Section for details of the synthesis). The volume ratio of DETA/H₂O showed a considerable influence on the morphology of loaded CoSe₂ (Supporting Information, Figure S3), and unique NG-CoSe₂-nanobelt composite can only be obtained at a ratio of 2:1. Hydrothermal reaction at 180 °C with the presence of suitable amount of DETA led to crystallization of CoSe₂ nanobelts and reduction of GO sheets,

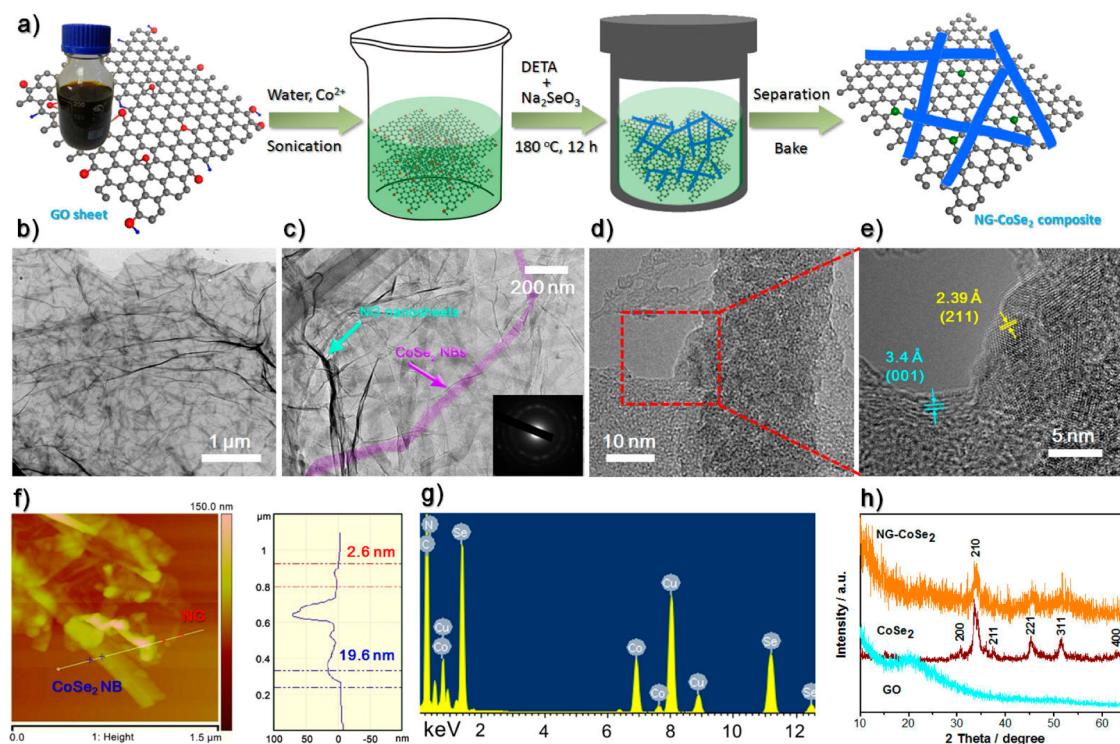


Figure 1. (a) Schematic illustration of the formation of the NG-CoSe₂ composite. (b–d) TEM images with different magnifications of NG-CoSe₂ composite. The inset in (c) shows the corresponding SAED pattern. (e) HRTEM image of a part of CoSe₂ nanobelt and its neighboring NG support taken on the marked part in (d). (f) AFM image and corresponding height profile of NG-CoSe₂ composite. (g) EDX spectrum and (h) XRD pattern of the composite catalyst.

forming the fluffy NG-CoSe₂ composite materials. The CoSe₂ loading amount in the composite was about 78.8 wt % based on the thermal-gravimetric measurement (Supporting Information, Figure S4).

Transmission electron microscopy (TEM) images (Figure 1b,c; also Supporting Information Figure S1) clearly show that very long belt-like materials (2–3 μ m) with flexible, thin, and almost transparent features are immobilized on large single NG sheets (>6 μ m). Selected area electron diffraction shows the polycrystalline nature of the composite, confirming the growth of CoSe₂ nanobelts on NG sheet (inset in Figure 1c and Supporting Information Figure S5). High-resolution TEM (HRTEM) study in Figure 1d,e reveals that the nanobelt surface is coarse and consists of many tiny particles (Supporting Information, Figure S6). The lattice fringe of a representative particle with *d*-spacing of 2.39 \AA can be assigned to the (211) plane of the cubic phase CoSe₂ (JCPDS 9-234). Additionally, Figure 1e also discloses the lattice fringe of connected support with a spacing of 3.4 \AA , which corresponds well to the (001) plane of graphene.⁴⁰ Note here that without GO sheets, the exact same synthesis strategy produced single-crystalline CoSe₂-DETA mesostructured nanobelts.³⁴ Such great structural change highlights the important role of GO sheets as a useful substrate for mediating the nucleation and growth of foreign materials. Atomic force microscopy (AFM) was used to characterize the topographic height of NG-CoSe₂ composite on mica (Figure 1f). The height profile in Figure 1f shows average heights of \sim 19.6 nm for CoSe₂ nanobelt and \sim 2.6 nm for NG sheet (about 2.6 times higher than single-layer graphene on mica substrate⁴¹). Energy-dispersive X-ray spectroscopy (EDS) shows that only C, N, Se, and Co can be detected in the composite with Cu peak emanating from the TEM grid (Figure 1g), eliminating other impure elements in the sample. X-ray diffraction (XRD) pattern in Figure 1 h further confirms the formation of NG-CoSe₂ composite, which is in line with the above HRTEM analysis.

The surface composition of GO and NG-CoSe₂ composite was characterized by X-ray photoelectron spectroscopy (XPS). Besides the appearance of expected Se and Co elements, the XPS survey spectrum for NG-CoSe₂ clearly reveals that significant content of N (\sim 19.36% atomic percent) is doped in graphene after the small-molecule-amine-assisted hydrothermal process (Figure 2a), in line with our recent work.⁴² The high-resolution N 1s spectrum of the NG-CoSe₂ in Figure 2b can be fitted to four peaks of pyridinic N (398.7 eV), C–N–C (399.5 eV), pyrrolic N (400.2 eV), and graphitic N (400.8 eV).^{42,43} High-resolution C 1s spectra of pure GO and NG-CoSe₂ composite are compared in Figure 2, panels c and d, which reveal a significant reduction of C–O peak at 286.7 eV, along with the appearance of a new C–N peak at 285.8 eV.⁴³ Such great changes indicate that the amine-assisted (here is

DETA) hydrothermal strategy is very efficient for the chemical reduction and N doping of GO simultaneously. The reduction of GO is further proved by Fourier transform infrared spectroscopy (FTIR) study shown in Figure 2e, where all the oxygen-containing groups are significantly reduced or entirely removed for the NG-CoSe₂ sample. Raman spectra of GO and NG-CoSe₂ composite all present a D band located around 1342 cm^{-1} (arises from the sp^3 defect sites) and a G band around 1570 cm^{-1} (arises from sp^2 -bonded pairs) as well as a 2D band located around 2680 cm^{-1} and a D + G band around 2910 cm^{-1} .⁴⁴ Although there is no clear change in the position of D and G bands, the I_D/I_G ratio of the NG-CoSe₂ composite did increase notably, suggesting the altered structure of GO originating from the introduction of defects by N-doping.⁴⁴

We then evaluated the electrochemical activity of this new NG-CoSe₂ composite for the OER. To this end, a film of as-synthesized NG-CoSe₂ composite was deposited onto glassy carbon (GC) electrode for cyclic voltammetry (CV) in O_2 -saturated 0.1 M KOH (see Experimental Section for details). As a reference point, similar measurements for commercial Pt/C catalyst (Johnson-Matthey, 20 wt %) and the state-of-the-art RuO₂ catalyst (Sigma-Aldrich) were also performed. The ohmic potential drop (iR) losses that arise from the solution resistance were all corrected (Supporting Information, Figure S7). In Figure 3a, the polarization curve from NG-CoSe₂ composite shows a much earlier OER onset potential (\sim 1.523 V versus the RHE) and greater catalytic current than those of pure CoSe₂ nanobelts and Pt/C reference. For RuO₂ catalyst, the OER current appears at a bit smaller onset potential of \sim 1.481 V (Figure 3a,c, Table 1). In sharp contrast, no obvious voltammetric responses were observed for the bare GC electrode and pure NG sheets (Figure 3a). The physical mixture of NG and CoSe₂ NBs (Supporting Information Figure S8) also exhibits the performance inferior to that of NG-CoSe₂ composite catalyst (Supporting Information Figure S9). It is very meaningful to compare the η requirements for achieving the current density of 10 mA cm^{-2} , which is a metric relevant to solar fuel synthesis.⁴⁵ Remarkably, the new NG-CoSe₂ composite can afford such current density at a small η of \sim 0.366 V, equating the η requirement for RuO₂ catalyst, and it is much smaller than those of pure CoSe₂ nanobelts and commercial Pt/C catalyst (Figure 3a,c, Table 1).

The OER kinetics of the above catalysts are probed by corresponding Tafel plots ($\log j - \eta$), as shown in Figure 3b. The resulting Tafel slopes are found to be \sim 40, \sim 69, \sim 66, and \sim 127 mV dec^{-1} for NG-CoSe₂ composite, commercial RuO₂, pure CoSe₂ nanobelts, and commercial Pt/C, respectively (Figure 3b,c, and Table 1). Note here that NG-CoSe₂ composite exhibits the smallest Tafel slope and is therefore the most

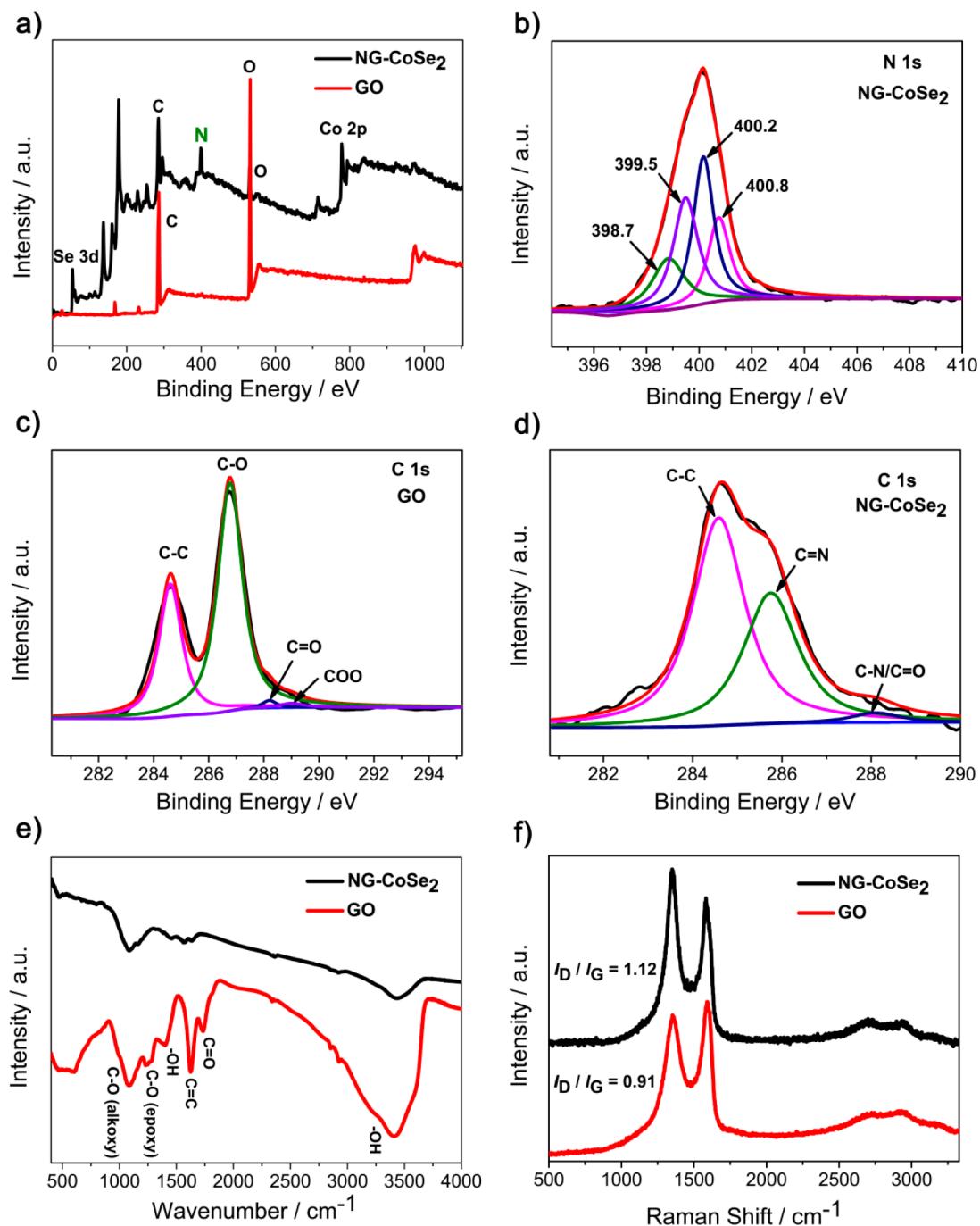


Figure 2. (a) XPS survey spectra of GO and NG-CoSe₂ composite. (b) High-resolution N 1s XPS spectrum of NG-CoSe₂ composite. (c and d) High-resolution C 1s spectra of (c) GO and (d) NG-CoSe₂ composite. (e) FTIR spectra of GO and NG-CoSe₂ composite. (f) Raman spectra of GO and NG-CoSe₂ composite.

efficient electrocatalyst among the studied materials. Such Tafel slope is also smaller than that of the well-investigated Co-based noble metal-free OER catalysts in the literature (Supporting Information, Table S1). It is interesting to note that the Tafel slope of 66 mV dec⁻¹ for pure CoSe₂ nanobelts is also smaller than that of RuO₂, suggesting the outstanding intrinsic OER kinetics of this kind of Co-based material even compared with RuO₂ catalyst. The further reduced Tafel slope of kinetic current down to a theoretical value of

40 mV dec⁻¹ ($2 \times 2.303RT/3F$, where R is the ideal gas constant, T is the absolute temperature, and F is the Faraday constant) for NG-CoSe₂ composite demonstrates the synergistic enhancement of OER activity taking effect in the composite.

To further assess their OER catalytic ability, the mass activity and turnover frequency (TOF) of above catalysts at a η of 0.366 V (η that needed to afford a current density of 10 mA cm⁻² for both NG-CoSe₂ composite and RuO₂) were also presented (Table 1).

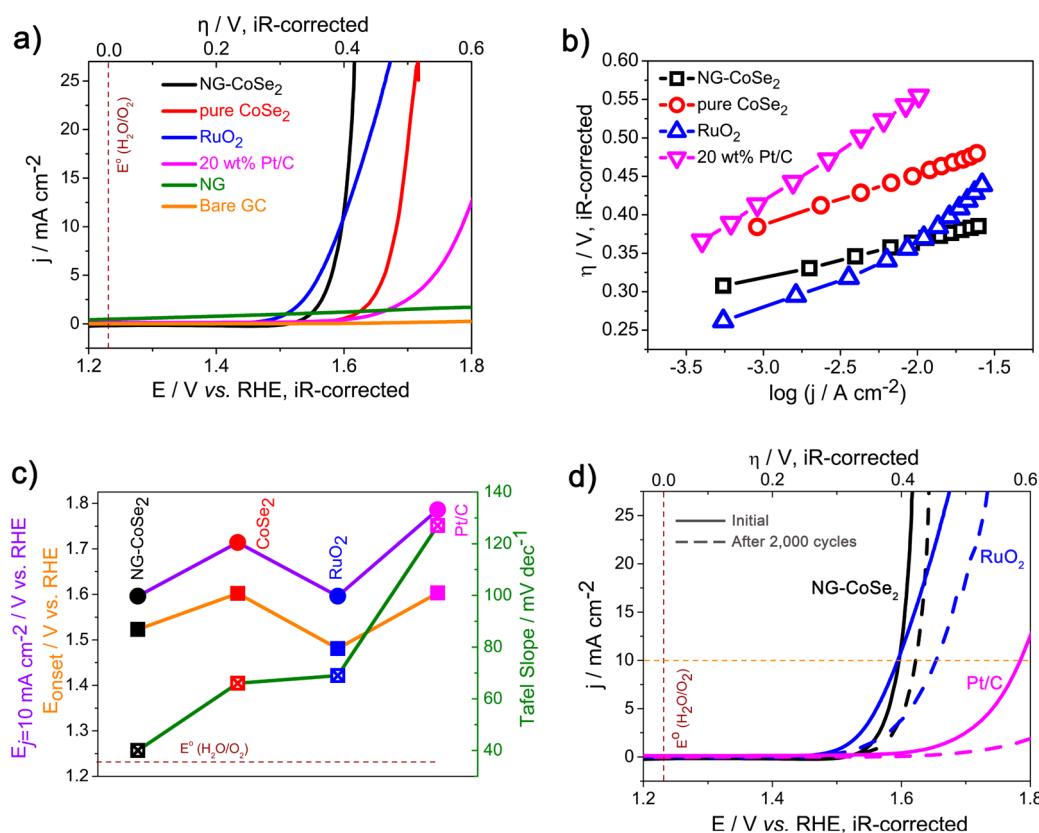


Figure 3. (a) Polarization curves for OER on bare GC electrode and modified GC electrodes comprising the NG sheets, commercial 20 wt % Pt/C and RuO₂ catalysts, pure CoSe₂ nanobelts, and NG-CoSe₂ composite. (b) Tafel plot (overpotential versus log current) derived from (a). (c) Comparison of Tafel slopes, onset potentials, and potentials required to reach $j = 10 \text{ mA cm}^{-2}$ for NG-CoSe₂ composite, pure CoSe₂ nanobelts, commercial RuO₂, and 20 wt % Pt/C catalysts. (d) OER polarization curves of NG-CoSe₂ composite, RuO₂, and 20 wt % Pt/C catalysts before and after potential sweeps (0.3–0.8 V versus Ag/AgCl) for 2000 cycles. All the measurements were performed in O₂-saturated 0.1 M KOH (pH ~13) at 5 mV s⁻¹ scan rate at 1600 rpm. The iR loss from the solution resistance was corrected. Catalyst loading: ~0.2 mg cm⁻².

TABLE 1. Comparison of OER Activity Data for Different Catalysts

catalyst	onset potential [V vs. RHE]	$\eta @ J = 10 \text{ mA cm}^{-2}$ [mV]	mass activity @ $\eta = 366 \text{ mV}$ [A g ⁻¹]	Tafel slope [mV dec ⁻¹]	TOF @ $\eta = 366 \text{ mV}$ [s ⁻¹] ^a
NG-CoSe ₂	1.523	366	63.45 ^b	40	0.03565 ^b
CoSe ₂	1.602	484	2.75	66	0.00773
RuO ₂	1.481	366	50.00	69	0.01724
20 wt % Pt/C	1.603	556	9.86 ^c	127	0.00505 ^c

^a The values of TOF were calculated by assuming that every metal atom are involved in the catalysis (lower bound, see Experimental Section for the calculated method).

^b Based on the amount of CoSe₂ (78.8 wt %). ^c Based on the amount of Pt (20 wt %).

The calculated mass activity for NG-CoSe₂ composite is 63.45 A g⁻¹, outperforming other studied catalysts even RuO₂ (Table 1). The intrinsic activities of above catalysts were estimated by TOF. The constructed new NG-CoSe₂ composite was found to exhibit the highest TOF of $\sim 3.565 \times 10^{-2} \text{ s}^{-1}$ on the assumption that every metal atom catalytically active (lower bound, Table 1).

Other than high activity, the long-term stability is another critical parameter that determines the practicability of electrocatalysts. To assess this, we performed continuous potential cycling between 1.26 and 1.76 V (versus RHE) for the NG-CoSe₂ composite with RuO₂ and Pt/C as references in O₂-saturated 0.1 M KOH. As shown in Figure 3d, after 2000 cycles, the NG-CoSe₂

catalyst needs a mere 25 mV increase in η to reach the current density of 10 mA cm⁻², while the same experiment leads to a 58 mV η increase for RuO₂ and a failure to reach such current density for Pt/C, demonstrating the superior durability of the new NG-CoSe₂ composite catalyst.

As noted above, pure N-doped graphene did not affect OER activity (Figure 3a). Therefore, it stands to reason that the exceptional OER activity of NG-CoSe₂ composite was originated from loaded CoSe₂ nanobelts, where NG served as a synergist. For well-studied cobalt oxides, it has been widely accepted that Co (IV) cations are critical to enable OER.^{9,12} The high valent Co cations were believed to enhance the electrophilicity

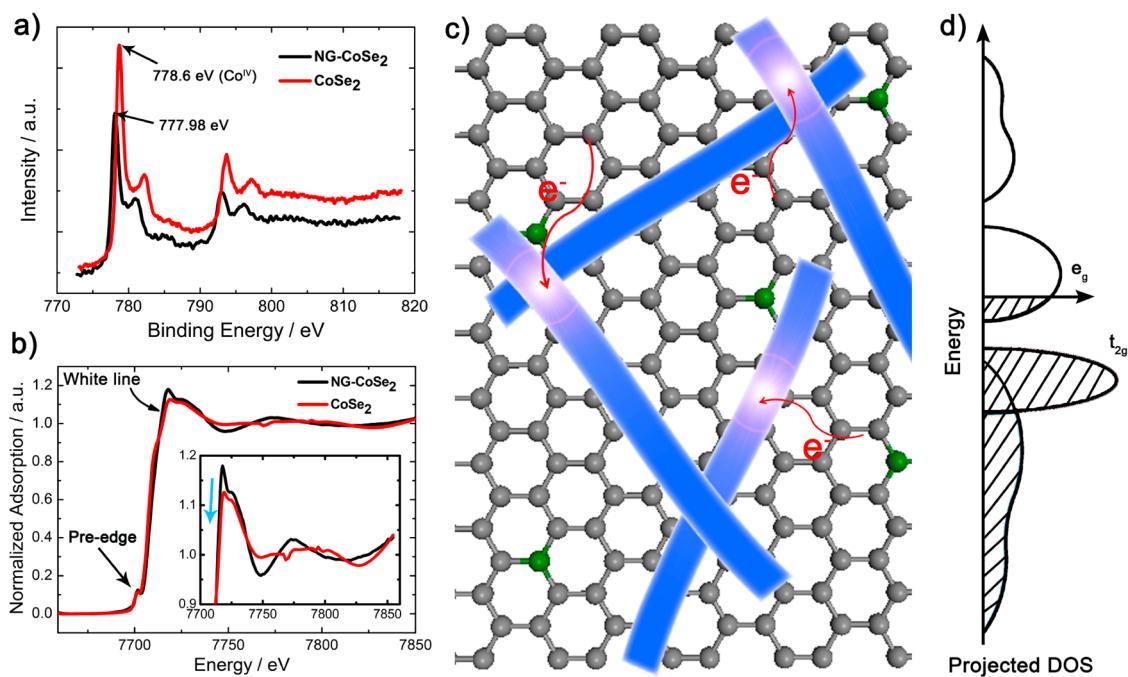


Figure 4. (a) High-resolution Co 2p XPS spectra for pure CoSe₂ nanobelts and NG-CoSe₂ composite. (b) Co K-edge XANES spectra for pure CoSe₂ nanobelts and NG-CoSe₂ composite. Inset in (b) is the enlarged region of peaks of Co K-edge XANES white line. (c) Schematic image demonstrates the electron donation from the NG to CoSe₂. Gray, green balls and blue belts correspond to C, N atoms and CoSe₂ nanobelts, respectively. (d) Schematic density-of-states (DOS) of CoSe₂, which is adapted from ref 50.

of adsorbed O, thus facilitate the formation of hydroperoxy (OOH) species and subsequent conversion to O₂ molecules.^{9,12} As to cubic phase CoSe₂, the surface Co (IV) cations (verified by the binding energy of Co 2p_{3/2} at 778.6 eV, Figure 4a) were also proven to be the cause of its observed OER activity.²⁴ However, the metal–oxygen interaction is not optimum. On the basis of the *d*-band theory, the catalytic activity of a material is in principle determined by the metal *d* states near the Fermi level.⁴⁶ For transition metal chalcogenides, the interaction between oxygen and metal *d* states is responsible for the OER activity. Because the e_g orbital of transition metal ions participates in σ -bonding with a surface-anion adsorbate, modulating the *d*-electron filling in e_g bands will optimize the bond strength of oxygen-related intermediate species (important for OER) on catalytic surface and thus foster performance optimization.³ The greatly improved OER performance of CoSe₂ nanobelts after growing on graphene indicates the modified electronic structure of CoSe₂ in the composite materials, which were gleaned by X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge spectra (XANES) measurements (Figure 4). Compared to pure CoSe₂ nanobelts, the electron binding energy of Co 2p for NG-CoSe₂ composite showed a ~0.62 eV decrease, corresponding to electron transfer from NG to CoSe₂ (Figure 4a,c).⁴⁷ Such electron donation was also confirmed by XANES. Figure 4b and the inset show the normalized XANES spectra collected at Co K-edge,

from which we can see an obvious increase in white line intensity after growing CoSe₂ on NG sheets, strongly indicating the electron transfer from NG to CoSe₂ (Figure 4c).^{48,49} As to the partially filled e_g bands (e_g < 1) of pyrite-type CoSe₂,⁵⁰ the surface-oxygen interaction is a bit strong for OER (Figure 4d). The electron donation from NG sheets to CoSe₂ will afford more e_g-filling in CoSe₂, which could weaken the surface-oxygen interaction to moderate bond strength (neither too strong nor too weak), thus greatly enhancing the OER kinetics. The optimized electronic structure of CoSe₂ after growing them on NG that leads to the improved OER activity can also be evidenced by the inferior performance of their physically mixed sample (Supporting Information Figures S8 and S9). Moreover, the NG sheets also endue the constructed composite catalyst with a high electrical conductivity. These advantages in the composite together are responsible for the synergistic OER catalytic activity.

CONCLUSIONS

In summary, we have successfully grown *in situ* CoSe₂ nanobelts on GO sheets to prepare a new N-doped graphene/CoSe₂ composite catalyst by using a simple small-molecule-amine-assisted hydrothermal strategy. This cheap and easily prepared electrocatalyst showed exceptional OER activity with a small η of 0.366 V at the current density of 10 mA cm⁻², large anodic currents, and a Tafel slope down to 40 mV dec⁻¹ in alkaline solution, which was found to approach or

compare favorably with the best performance of well-studied Co-based materials and the commercial RuO₂ catalyst. The NG-CoSe₂ catalyst also exhibited outstanding durability under harsh OER cycling conditions. The synergism between the N-doped reduced graphene and

CoSe₂ nanobelts is believed to boost the excellent OER performance. Our study raises great promises for designing effective OER electrocatalysts by suitable electrical and chemical coupling of cheap functional materials, which is highly request for a viable hydrogen economy.

EXPERIMENTAL SECTION

Materials. All chemicals are of analytical grade and were used as received without further purification.

Synthesis of Graphene Oxide (GO) Sheets. GO was prepared by chemical oxidation and exfoliation of graphite flakes (Sigma-Aldrich) under acidic conditions according to the Hummers' method.³⁹ The obtained GO was washed thoroughly and redispersed in deionized water (DIW) to harvest final GO DIW suspension with a concentration of $\sim 0.3 \text{ mg mL}^{-1}$ (the concentration of the GO stock suspension was determined by measuring the mass of the GO lyophilized from a given volume of the suspension).

Synthesis of NG-CoSe₂ Composite. In a typical procedure, 1 mmol (0.249 g) of Co(AC)₂·H₂O was added into 13 mL of GO DIW suspension under magnetic stirring. About 10 min later, 26 mL of DETA (diethylenetriamine) and 1 mmol (0.173 g) of Na₂SeO₃ were added. After further stirring for 0.5 h in a beaker to dissolve completely, the homogeneous solution was transferred into a 50 mL Teflon-lined autoclave, which was sealed and maintained at 180 °C for 12 h and then naturally cooled to room temperature. The resulting solid product was collected and washed with DIW. Then, the nanocomposite powder was obtained by freeze-drying for next characterizations.

Synthesis of N-Doped Reduced Graphene (NG) and Pure CoSe₂ Nanobelts. The synthetic procedure of NG is the same with that for preparing NG-CoSe₂, the only difference is that no Co(AC)₂·H₂O and Na₂SeO₃ were added during the synthesis. Pure CoSe₂ nanobelts were also made through the same procedures as preparing NG-CoSe₂, the only difference is that GO DIW suspension was replaced by pure DIW.

Materials Characterization. The samples were characterized by different analytic techniques. X-ray powder diffraction (XRD) was carried out on a Rigaku D/max-rA X-ray diffractometer with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$); TEM images, HRTEM images, selected-area electron diffraction (SAED), and an Energy-disperse X-ray spectrum (EDS) were taken with a JEOJ-2010 transmission electron microscope with an acceleration voltage of 200 kV. An atomic force microscope (Nanoscope IIIa; Digital Instruments) was used to measure the morphology of the sample. A Si tip (Nanoprobe, Digital Instruments, Inc.) was used in the tap mode. The X-ray photoelectron spectra (XPS) were recorded on an ESCALab MKII X-ray photoelectron spectrometer using Mg K α radiation exciting source. The Fourier transform infrared (FTIR) spectra were measured on a Bruker Vector-22 FT-IR spectrometer at room temperature. Raman spectroscopy was carried out on a JY LABRAM-HR confocal laser micro-Raman spectrometer using Ar⁺ laser excitation with a wavelength of 514.5 nm. Thermal gravimetric analysis (TGA) was carried out on a Perkin-Elmer Diamond TG/DTA thermal analyzer with a heating rate of 10 °C·min⁻¹ and a flowing N₂ of 50 mL·min⁻¹.

Electrocatalytic Study. Electrochemical measurements were performed at room temperature using a rotating disk working electrode made of glassy carbon (PINE, 5 mm diameter, 0.196 cm²) connected to a Multipotentiostat (IM6ex, ZAHNER elektrik, Germany). The glassy carbon electrode was polished to a mirror finish (No. 40-6365-006, Gamma Micropolish Alumina, Buehler; No. 40-7212, Microcloth, Buehler) and thoroughly cleaned before use. Pt wire and Ag/AgCl (PINE, 4 M KCl) were used as counter and reference electrodes, respectively. The potentials reported in our work were *versus* the reversible hydrogen electrode (RHE) through RHE calibration described below.

The preparation method of the working electrodes containing investigated catalysts can be found as follows. In short, 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 %, Sigma-Aldrich), and then the mixture was ultrasonicated for about 1 h to generate a homogeneous ink. Next, 8 μL of the dispersion was transferred onto the glassy carbon disk, leading to the catalyst loading $\sim 0.2 \text{ mg cm}^{-2}$. Finally, the as-prepared catalyst film was dried at room temperature. For comparison, bare glassy carbon electrode which has been polished and cleaned was also dried for electrochemical measurement.

Before the electrochemical measurement, the electrolyte (0.1 M KOH, 99.99% metal purity, pH ~ 13) was degassed by bubbling oxygen for at least 30 min to ensure the H₂O/O₂ equilibrium at 1.23 V *versus* RHE at a rotation rate of 1600 rpm. The polarization curves were obtained by sweeping the potential from 0 to 1 V *versus* Ag/AgCl at room temperature and 1600 rpm, with a sweep rate of 5 mV s⁻¹. The cyclic voltammetry (CV) curves were obtained by sweeping the potential from -0.2 to 1 V *versus* Ag/AgCl at room temperature and 1600 rpm. All the data were recorded after applying a number of potential sweeps until which were stable.

The accelerated stability tests were performed in O₂-saturated 0.1 M KOH at room temperature by potential cycling between 0.3 and 0.8 V *versus* Ag/AgCl at a sweep rate of 100 mV/s for 2000 cycles. At the end of the cycles, the resulting electrodes were used for polarization curves at a sweep rate of 5 mV/s.

RHE Calibration. In all measurements, we used Ag/AgCl (PINE, 4 M KCl) as the reference electrode. It was calibrated with respect to RHE. The calibration was performed in the high purity hydrogen saturated electrolyte with a Pt foil as the working electrode. Cyclic voltammetry (CV) was run at a scan rate of 1 mV s⁻¹, and the average of the two potentials at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reaction. In 0.1 M KOH solution, $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.96 \text{ V}$.

Calculation method. Details concerning the calculation of mass activity and turnover frequency (TOF) are shown below:

The values of mass activity (A g⁻¹) were calculated from the catalyst loading m (0.2 mg cm⁻²) and the measured current density j (mA cm⁻²) at $\eta = 0.336 \text{ V}$:

$$\text{Mass activity} = \frac{j}{m} \quad (1)$$

The values of TOF were calculated by assuming that every metal atom is involved in the catalysis (lower TOF limits were calculated):

$$\text{TOF} = \frac{j \times S}{4 \times F \times n} \quad (2)$$

Here, j (mA cm⁻²) is the measured current density at $\eta = 0.336 \text{ V}$, S (0.196 cm²) is the surface area of glassy carbon disk, the number 4 means 4 electrons/mol of O₂, F is Faraday's constant (96485.3 C mol⁻¹), and n is the moles of coated metal atom on the electrode calculated from m and the molecular weight of the coated catalysts.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: additional TEM and HRTEM images, TGA curve, and iR-correction. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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