Carbon-Nanotube-Incorporated Graphene Scroll-Sheet Conjoined Aerogels for Efficient Hydrogen Evolution Reaction

Yiqin Shi,* Wei Gao,‡ Hengyi Lu,* Yunpeng Huang,‡ Lizeng Zuo,* Wei Fan,*†‡ and Tianxi Liu*†‡

Introduction

Hydrogen, as one of the most promising sustainable energy carrier to substitute fossil fuels, has drawn tremendous attentions. Splitting water by using electricity is a green way to produce hydrogen. Although platinum (Pt)-based material is most effective in electrocatalyzing hydrogen evolution reaction (HER), the high cost and scarcity of Pt has driven the research on exploring earth-abundant and high performance electrocatalysts. Coupling MoSe₂ nanosheets with carbon aerogel, possessing large surface area and excellent electrical conductivity, could perform as good template for the optimization of HER performance of TMDs. Various methods like chemical vapor deposition (CVD), hydro-thermal, direct ink writing and ascorbic reduction have been employed to manufacture graphene-based aerogels. However, these methods either require template with hard accessibility or could achieve aerogels in which graphene sheets could not be exposed to reactants. The integration of MoSe₂ with carbon substrates like carbon nanotubes, graphene, carbon fiber cloth or cotton-derived carbon fiber aerogel could promote its catalytic performance.

ABSTRACT: Developing low-cost Pt-free hydrogen evolution reaction (HER) electrocatalyst is highly desired in exploiting hydrogen as a sustainable energy carrier. Herein, hierarchically structured graphene-carbon nanotube aerogel-MoSe₂ hybrid (GCA-MoSe₂) was constructed as efficient HER electrocatalysts. GCA was facilely fabricated by direct freeze-drying of graphene oxide (GO)-carbon nanotube (CNT) hybrid dispersion, with subsequent carbonization. Through a shock cooling method, a unique scroll-sheet conjoined architecture could be formed in GCA, which can function as highly conductive skeleton, thus facilitating the transport of electrons through the whole hybrids. Furthermore, CNT’s acting as “spacers” between graphene layers can efficiently impede their restacking, thus giving full play to the superior electrical conductivity of graphene. The hierarchical porous aerogel skeleton could allow full impregnation of electrolyte, accelerating the ion diffusion kinetics. Benefiting from the three-dimensional (3D) network of GCA, MoSe₂ nanosheets can grow densely and perpendicularly on the aerogel, preventing them from aggregation to maximize the number of catalytic active sites on the edges. The ensemble of these benefits makes the hybrid an efficient electrocatalyst for HER, which exhibits an onset potential of 113 mV, small Tafel slope of 68 mV decade⁻¹ and good stability. Such a simple method of immobilizing guest nanosheets/particles in the host of GCA opens a new avenue for manufacturing macroscopic electrode materials in large scale.

KEYWORDS: MoSe₂, Graphene-carbon nanotube aerogel, Scroll-sheet conjoined, Hydrogen evolution reaction
usually stack to form thick slabs between the macropores, leaving behind inner layers inaccessible to electrolyte. Other carbon nanomaterials like one-dimensional carbon nanotubes (CNTs) have been previously introduced to act as spacers to prevent graphene from restacking. Incorporation of CNTs into aerogel can space the graphene layers with additional mesopores to allow more complete impregnation of electrolyte, thus improving the electrochemical performance.23,24 Recently, graphene scrolls have been reported to be prepared by rolling graphene sheets, with enhanced physicochemical properties.25,26,27 Graphene scrolls display similar tubular structure as graphene sheets, with enhanced physicochemical properties.26,27 Graphene scrolls have been reported to be prepared by rolling graphene sheets, with enhanced physicochemical properties.23,24 Incorporation of CNTs into the graphene backbone could alleviate the restacking of graphene layers and further enhance the conductivity of the whole structure. By a solvothermal process, MoSe2 nanosheets are vertically immobilized on the all-carbon framework, fully exposing abundant active edge sites to the electrolyte while the underlying GCA could facilitate the ion/electron transport. The resultant GCA-MoSe2 hybrid could be used as an efficient electrocatalyst for HER. The performance was measured by linear sweep voltammetry (LSV) curves and cycling test was also conducted to verify its stability in acidic media.

**EXPERIMENTAL SECTION**

**Materials.** Multiwalled carbon nanotubes (MWCNTs) (diameter = 30–50 nm) were obtained from Chengdu Organic Chemicals Co., Ltd., synthesized by the CVD method. H2SO4 (95–98%), H2O2 (30%), HNO3 (65%), N,N-dimethylformamide (DMF, ≥99.5%), ethanol, glucose, potassium permanganate (KMnO4), sodium molybdate dihydrate (Na2MoO4·4H2O) (99.99%), selenium (Se) powder, and hydrazine hydrate (N2H4·H2O, 50 wt % in water) were purchased from Sinopharm Chemical Reagent Co., Ltd. Natural graphite powder (325 mesh) was purchased from Alfa-Aesar (Ward Hill, MA) and used without further purification. Deionized (DI) water was used throughout the experiments. All chemicals were analytic grade and used without further purification.

**Preparation of Graphene–Carbon Nanotube Aerogel (GCA).** Graphite oxide was dispersed in DI water with sonication to form 8 mg mL−1 graphite oxide (GO) dispersion. CNTs were acidized by the mixture of HNO3/H2SO4 (volume ratio = 1:3) at 70 °C for 2 h, and then dispersed in DI water to form 4 mg mL−1 dispersion. The above two dispersions of GO and CNTs were mixed together under vigorous stirring with volume ratio of 1:1 and poured into 7 mL centrifuge tube. The centrifuge tube was immersed in liquid nitrogen and the dispersion was frozen rapidly by the shock cooling. After subsequent lyophilization, GO–CNT aerogel (GOCA) was obtained and then placed in a tubular furnace for carbonization under nitrogen flow at 800 °C for 2 h with a heating rate of 5 °C min−1. After naturally cooling down to room temperature, GCA was obtained.

**Preparation of GCA-MoSe2 Hybrids.** The synthetic procedure of GCA-MoSe2 hybrids by a one-pot solvothermal reaction method is illustrated in Scheme 1. 150 mg of selenium (Se) powder was dispersed in 50 mL of hydrazine hydrate via vigorous stirring to obtain 3 mg mL−1 Se dispersion and then heated at 80 °C for 1 h. A certain amount of Na2MoO4 was added into 15 mL DMF, and Se dispersion was dropwise added into the above DMF solution with a Mo/Se molar ratio of 1:2. GCA was sliced into pieces with mass of 10 mg and immersed into the precursor solution, followed by transferring to 40 mL Teflon autoclave and reacting at 180 °C for 12 h. Afterward, the as-obtained GCA-MoSe2 hybrid was collected and washed with DI water for several times. After freeze-drying, the final product was obtained by annealing at 450 °C for 2 h with a ramping rate of 5 °C min−1 to increase the crystallinity of MoSe2 nanosheets. To achieve GCA-MoSe2 hybrids with different loading of MoSe2, 15, 30, and 60 mg of Se were added respectively, and the corresponding final products were denoted as GCA-MoSe2-1, GCA-MoSe2-2, and GCA-MoSe2-3.

For comparison, pure MoSe2 was prepared without adding GCA to the precursor solution. Graphene aerogel–MoSe2 (GA-MoSe2) hybrid was prepared by using GA to substitute GCA as supporting material, which was prepared by shock cooling of neat GO dispersion (4 mg mL−1) using liquid nitrogen.

**Characterization.** Raman spectra were performed on a JobinYvon XploRA Raman spectrometer at an exciting wavelength of 632.8 nm. The morphology of samples was characterized by field emission scanning microscopy (FESEM) (Ultra 55, Zesis) at an acceleration voltage of 5 kV, and the chemical composition was studied by energy dispersive X-ray spectroscopy (EDX). Transmission electron microscopy (TEM) observations were conducted by JEOL JEM 2100 TEM under an acceleration voltage of 200 kV. Samples for TEM observations were prepared by dropping solution on the copper grids followed by drying. The crystalline structure was characterized by X-ray diffraction (XRD) conducted on an X’Pert Pro X-ray diffractometer with Cu Kα radiation (λ = 0.1542 nm) under a current of 40 mA and a voltage of 40 kV with 2θ ranges from 5° to 80°. X-ray photoelectron spectroscopy (XPS) analysis was performed with a VG ESCALAB 220i-XL device and all XPS spectra were corrected using C 1s line at 284.5 eV. In addition, the curve fitting and background subtraction were accomplished using XPS PEAK41 software.

**Electrochemical Measurements.** Prior to all the hydrogen evolution experiments, glassy carbon electrodes (GCE) (diameter = 3 mm) were pretreated according to the previous report.70 The working electrode was prepared as follows: 2 mg of GCA-MoSe2 hybrid was...
dispersed in 1 mL DMF/DI water mixed solution (volume ratio = 2:1) containing 20 μL 5 wt% Nafion. After being sonicated for 2 h, 8 μL of the as-obtained slurry was dropped onto GCE and dried at room temperature to achieve GCA-MoSe₂ hybrid modified GCE.

All electrochemical tests were performed in a standard three-electrode setup using CHI 660D electrochemical workstation (Chenhua Instruments Co, Shanghai, China) at room temperature, where sample modified GCE was applied as the working electrode, saturated calomel electrode (SCE) as the reference electrode and graphite rod as counter electrode. The electrocatalysis of samples toward HER was carried out by liner sweep voltammetry (LSV) in nitrogen purged 0.5 M H₂SO₄ with scan rate of 2 mV s⁻¹ toward HER was carried out by liner sweep voltammetry (LSV) in nitrogen purged 0.5 M H₂SO₄ with scan rate of 2 mV s⁻¹. Electrochemical Impedance spectroscopy (EIS) measurements were conducted in 0.5 M H₂SO₄ from 0.01 to 100 Hz at a potential of 200 mV vs RHE with the amplitude of 5 mV. The cycling stability was investigated by cyclic voltammetry (CV) between −0.35 and 0.25 V vs RHE at a scan rate of 100 mV s⁻¹. In all electrochemical tests, the potentials were calibrated to RHE according to the equation of $E_{RHE} = E_{SCE} + (0.241 + 0.059 \text{pH})$ V.

RESULTS AND DISCUSSION

Morphology and Structure of GCA-MoSe₂ Hybrids. GOCA was fabricated by direct shock cooling of the GO/CNT mixed aqueous dispersion. However, pure CNTs could not self-assemble to form aerogel by the same shock cooling procedure. Only when GO was added as cross-linking agent, the aerogel could form and be shaped up by the vessel. The as-obtained GOCA displays black color, which is distinctly different from the brown color of GO aerogel prepared in the absence of CNTs (Figure S1A). The inner structure of GCA is a 3D network conjoined by graphene scrolls and sheets (Figure 1A). This unique morphology is induced by the shock cooling effect of liquid nitrogen. In this process, the shrinkage of graphene layers occurs and drive flat GO sheets to roll up into scrolls, which is a more energetically favorable state. These scrolls assemble with adjacent layers to form a 3D network. The calcination in the final step can reduce GO to graphene, as well as remove the oxygen containing groups in CNTs, while the scroll-sheet conjoined network could be well retained. In the microscopic structure, the existence of scrolls can prohibit graphene sheets from severely restacking, and lead to generation of macropores. CNTs coexist with graphene in two forms: intercalating between the graphene sheets (Figure 1B) or being enwrapped by the tubular graphene scrolls (Figure 1C). TEM images further reveal that the thin graphene layers are partially rolled to form the unique scroll-sheet conjoining structure (Figure 1D). CNTs were observed to interconnect with each other and evenly adhere to graphene wall in both cases (Figure 1E and 1F). The uniform hybridization of graphene and CNTs is derived from the homogeneous dispersion of GO and CNTs through the π-π interactions in precursor dispersion. The GOCA was converted into GCA by the high temperature calcination. From the Raman spectra presented in Figure S1B, G band and D band were observed for both GOCA and GCA. For GOCA, the intensity ratio of D band ($I_D$) to G band ($I_G$) is 0.99, and the value is estimated to be 1.04 for GOCA, evidencing the reduction of GO by calcination. In addition, the all-carbon framework shows a nearly complete recovery after more than 50% compression as 1800 times of its bulk weight is imposed on (Figure S1C). This high compressibility can be attributed to the reinforcement of incorporated CNTs on relatively flexible graphene, which endow the scroll-sheet conjoined structure with intrinsic elasticity and elastic buckling under pressure. Furthermore, either attaching on the graphene sheets or being enwrapped by the graphene scrolls, the CNTs intertwining with each other could enhance the conductivity (5 S m⁻¹ for GA, 12 S m⁻¹ for GCA) and provide faster electron transfer pathway. The insertion or intercalation of CNTs between graphene interlayers can further hinder the restacking of graphene layers in these isolated sheets or scrolls and produce some mesopores. The hierarchical porous structure of CNTs incorporated graphene aerogel could also provide more regions for the growth of MoSe₂ nanosheets while the simplicity of this shock cooling method make it accessible for large-scale production.

Without any template for growing, pure MoSe₂ tends to form irregular shaped agglomerates with sizes of several micrometers (Figure S2A, S2B). When GCA serves as template for in situ growth of MoSe₂, ultrathin vertically oriented nanosheets can be anchored on the carbon skeleton (Figure 2A). With a proper
loading of MoSe2 nanosheets, the robust 3D scroll-sheet conjoined architecture was well retained without any collapse or blocking of the pores. From the high-magnification SEM images in Figure 2B and 2C, it is seen that MoSe2 is uniformly distributed on the graphene scrolls as well as the graphene sheets, maximizing its active edges. The EDX results taken from MoSe2 anchored graphene scrolls could further prove the even distribution of MoSe2 nanosheets on the carbon framework (Figure 2D−H). The atom ratio of Se to Mo evaluated from EDX spectrum is 2.15:1, which is very close to that (2:1) of MoSe2. From the TEM image, it is clearly observed that in the hybrid structure, CNTs tangling with each other are enwrapped by graphene scrolls (Figure 3A), while MoSe2 nanosheets are anchored on the outer wall of graphene scrolls, displaying a few-layered structure (Figure 3B). The interlayer spacing approximates 0.65 nm, which falls into the typical value of layered MoSe2.30 And the lattice fringe is measured to be 0.28 nm, which corresponds to the (100) face of the MoSe2 crystal.31

XRD pattern of pure GCA displays a peak centered at 2θ = 26.4°, which can be assigned to the (002) plane of stacked carbon sheets. For GCA-MoSe2-2 and GA-MoSe2, four other sharp peaks at 2θ = 13.0°, 31.1°, 37.4°, and 56.3° can also be observed and indexed to the (002), (100), (103), and (110) diffraction planes of hexagonal MoSe2, respectively, which is the same as pure MoSe2 (Figure 4). The XRD results confirm the successful anchoring of MoSe2 nanosheets on the supporting material of GCA or GA with good crystallinity after annealing. XPS spectra were measured to study the composition and surface chemical state of GCA-MoSe2. From the survey spectrum of GCA-MoSe2-2, C, Se, and Mo are observed as main elements coexisting in the hybrid (Figure 5A). The high

Figure 2. FESEM image of (A) GCA-MoSe2-2, and images of MoSe2 nanosheets grown vertically on (B) graphene sheet and (C) graphene scroll in the aerogel structure, respectively. High magnification FESEM image of (D) GCA-MoSe2-2 and (E) EDX spectrum taken from corresponding area and the elemental mapping for (F) Se, (G) Mo, (H) C.

Figure 3. TEM images of GCA-MoSe2-2 at (A) low and (B) high magnifications.

Figure 4. XRD patterns of GCA, pure MoSe2, GCA-MoSe2-2, and GA-MoSe2.
resolution Mo 3d spectrum can be deconvoluted into two peaks centered at 229.5 and 232.6 eV, which belong to Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$, respectively, revealing the chemical state of Mo$^{4+}$ in GCA-MoSe$_2$-2 (Figure 5B). The high resolution spectrum of Se 3d shows two peaks of Se 3d$_{5/2}$ and Se 3d$_{3/2}$, with the binding energy at 56.3 and 55.0 eV (Figure 5C), while the spectrum of Se 3p can be deconvoluted into peaks at 162.0 and 167.6 eV, which could be attributed to Se 3p$_{1/2}$ and Se 3p$_{3/2}$ (Figure 5D), all indicating the valence state of $-$2 for Se in the hybrid.

**Electrocatalytic Activity of GCA-MoSe$_2$ toward HER.**

The electrocatalytic activities of GCA-MoSe$_2$ hybrids toward HER were investigated using a three-electrode setup in the electrolyte of 0.5 M H$_2$SO$_4$. LSV curves of GCA, pure MoSe$_2$, GCA-MoSe$_2$-2, and GA-MoSe$_2$ were all measured and presented in Figure 6A. GCA displays no catalytic activity toward HER as its LSV curve almost approaches a horizontal line. Pure MoSe$_2$, GCA-MoSe$_2$, and GA-MoSe$_2$ all show distinct catalytic activity according to their LSV curves, indicating MoSe$_2$ is the core catalytic material in the hybrid. For bulk MoSe$_2$, the tendency of aggregation hinders the electrocatalytic activity. When GCA serves as support for anchoring MoSe$_2$ nanosheets, the HER performance can be dramatically promoted, which is manifested by a shift of onset potential from 198 mV to 113 mV, and less energy for driving a current density of 10 mA cm$^{-2}$ (an overpotential of 297 mV for MoSe$_2$ while only 228 mV for GCA-MoSe$_2$). As the basal edges of MoSe$_2$ have been identified as catalytic active sites for HER, the perpendicularly grown MoSe$_2$ nanosheets could not only maximize the active sites, but also facilitate ion/electrolyte transport at the electrode interface. The all-carbon aerogel performing as supporting material could minimize the aggregation and restacking of the MoSe$_2$ nanosheets, and also improve the electrical contact between electrocatalyst and the electrode with its intrinsic scroll-sheet conjoining conductive network. The graphene scrolls interconnect graphene sheets, inhibiting them from restacking, thus exposing more surface area for anchoring MoSe$_2$ nanosheets. Furthermore, this scroll-sheet conjoining structure could leave macropores in the hybrid, enabling full impregnation of electrolyte, thus improving the HER catalytic behavior. The improved electrochemical active surface area (ECSA) of GCA-MoSe$_2$ is further confirmed by the double layer capacitance ($C_{dl}$). $C_{dl}$ was measured by cyclic voltammetry (Figure 6C, 6D) in the potential range with no faradaic response for both GCA-MoSe$_2$-2 and pure MoSe$_2$. The $C_{dl}$ of GCA-MoSe$_2$-2 is estimated to be 1.31 mF cm$^{-2}$, which is more than 2-fold of that of pure MoSe$_2$ (0.51 mF cm$^{-2}$), indicating that the ECSA of GCA-MoSe$_2$-2 is greatly enhanced compared with pure MoSe$_2$ (Figure S3A, S3B). It is worth noting that GCA-MoSe$_2$-2 shows superior HER catalytic performance than GA-MoSe$_2$, as the latter shows higher onset potential and lower current density at the same overpotential. Evidently, the great difference of the HER performance between the two hybrids is caused by the incorporation of CNTs into the graphene scroll-sheet conjoined network. CNTs, displaying a 1D tubular structure, could enable a more accessible electrolyte contact by the spacing effect and enhance the conductivity by shortening the electron transport pathway, contributing to improved HER performance.

The loading amount of MoSe$_2$, which is controllable by tuning the addition amount of Se and Na$_2$MoO$_4$ also has a great influence on the HER electrocatalytic activity of GCA-MoSe$_2$. As indicated by the LSV curves in Figure S4, among all the three samples, GCA-MoSe$_2$-2, presents the most outstanding HER electrocatalytic activity since it displays a more positive onset potential and higher current density at the same overpotential in the LSV curve than the other two. GCA-MoSe$_2$-2 displays a well-defined hierarchical structure where few-layered MoSe$_2$ nanosheets are vertically grown on scroll-
sheet conjoined skeleton with a fine coverage, maximizing the exposed catalytic active sites. For GCA-MoSe2-1 prepared with 15 mg of Se, MoSe2 nanosheets with smaller size were sparsely immobilized on the GCA, and the embossing sketch of CNTs attached on graphene surface beneath the thin coverage of MoSe2 could even be observed (Figure S5A, S5B). The less loading amount of MoSe2 results in less active edges being exposed for electrocatalysis. While for GCA-MoSe2-3, the overloading of MoSe2 causes severe aggregation, leading to loss of active edges. Furthermore, the overgrowth of MoSe2 nanosheets goes toward the pore regions, causing the breaking of the porous structure (Figure S5C, S5D). Therefore, proper loading of MoSe2 on the carbon support could render optimized HER catalytic performance for GCA-MoSe2-2.

Tafel plots are extracted from the LSV curves for quantitative analysis of HER performance of different samples as shown in Figure 6B. The Tafel plots are well fitted to the Tafel equation, \( \eta = b \log(j) + a \), where \( \eta \) is the overpotential, \( j \) is the current density, and \( b \) is the Tafel slope. For pure MoSe2, GCA-MoSe2-2, and Pt, the Tafel slope is calculated to be 72, 68, and 31 mV decade\(^{-1}\), respectively. The decreased Tafel slope of GCA-MoSe2-2 compared with pure MoSe2 suggests less activation energy for electrocatalytic reaction, which can be ascribed to the confined growth of MoSe2 nanosheets onto GCA so that perpendicularly oriented, uniformly distributed and thereby edge-rich morphologies are formed for the GCA-MoSe2-2 hybrid. The Tafel slope of 68 mV decade\(^{-1}\) for GCA-MoSe2-2 suggests that HER proceeds by a Volmer-Heyrovsky mechanism where a rapid discharge step (the Volmer reaction) comes first and a rate-limiting electrochemical desorption step (the Heyrovsky reaction) follows up. The catalytic performance of GCA-MoSe2-2 prepared by us is comparable or superior to other previous reported MoSe2 based electrocatalysts (Table 1). This result further highlights the important role of GCA as template for anchoring MoSe2 nanosheets and enabling abundant active edges being exposed to the electrolyte. This

Figure 6. (A) LSV polarization curves for GCA, MoSe2, GA-MoSe2, and GCA-MoSe2-2 modified GCE in N₂-purged 0.5 M H₂SO₄ solution. Scan rate: 2 mV s\(^{-1}\). (B) Tafel plots for pure MoSe2, GCA-MoSe2, and Pt modified GCE. (C) CV curves of GCA-MoSe2-2 in the region of 0.1–0.3 V vs RHE at scan rate of 50, 100, 150, 200, 250, 300 mV s\(^{-1}\). (D) Plot showing the extraction of the double layer capacitance (\( C_dl \)) of GCA-MoSe2-2 at 0.2 V vs RHE. (E) Nyquist plots for MoSe2, GCA-MoSe2, and GA-MoSe2 at a potential of −200 mV vs RHE. (F) i-t curve for GA-MoSe2-2 modified GCE.
facilely fabricated all carbon scroll-sheet conjoined 3D skeleton derived from graphene-CNTs hybrids demonstrates its unique advantage by offering a fast electron transfer pathway which is beneficial to the electrocatalytic activity.

EIS tests were conducted for pure MoSe₂, GCA-MoSe₂, and GA-MoSe₂. The Nyquist plots indicate that GCA-MoSe₂ has smaller charge transfer resistance (Rct) of 100 Ω, than those of pure MoSe₂ and GA-MoSe₂ (Figure 6E). The EIS results supply to verify the enhanced Faradaic process and thus improved HER kinetics of the hybrid by coupling MoSe₂ with GCA. The durability of GCA-MoSe₂ hybrid is investigated via carrying out continuous electrocatalytic HER performance at a constant overpotential (Figure 6F). It can be observed that the current density exhibits only a slight attenuation after cycling for 20000 s, revealing the long-term stability of GCA-MoSe₂ electrocatalyst. The fluctuation of the curve is mainly due to the alternate accumulation and release processes of produced H₂ (g) bubbles that occur fiercely on the surface of the electrode material, indicating the rapid depletion of H⁺ in electrolyte, which may result in the degradation in current density. The LSV curve of GCA-MoSe₂ hybrid almost overlaps with the initial one after continuously 3000 CV cycles, with only very slight left shift, further confirming that the catalyst is highly stable (Figure 7A). The good stability of GCA-MoSe₂ electrocatalyst can be attributed to its robust morphology that keeps well during the violent hydrogen evolution reaction (Figure 7B).

Table 1. Comparison of the HER Performance of Different MoSe₂-Based Catalysts

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<th>Tafel slope (mV dec⁻¹)</th>
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Figure 7. (A) LSV polarization curves for GA-MoSe₂-2 modified GCE recorded before and after 3000 times of CV cycle. (B) SEM image of GA-MoSe₂-2 after cycling test.

CONCLUSIONS

In conclusion, GCA with unique scroll-sheet conjoined structure has been prepared via a simple liquid nitrogen shock cooling method. The as-obtained GCA exhibiting porous microscopic structure as well as macroscopic elasticity was used as substrate for the immobilization of MoSe₂ nanosheets through a solvothermal procedure. The hierarchically structured GCA-MoSe₂ with proper and uniform loading of MoSe₂ nanosheets on the all-carbon skeleton can render abundant active sites exposed to the electrolyte for catalyzing HER process. The unique CNTs incorporated scroll-sheet conjoined graphene aerogel also enables full impregnation of electrolyte into the electrode material and affords high conductivity for ion diffusion and electron transfer. The ensemble of these properties makes GCA-MoSe₂ hybrid potential candidate for HER electrocatalysis. The facilely prepared and well-designed GCA could be extended to immobilize other guest materials for a vast variety of applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b01181.

Digital image of GA, GCA, and CNTs and corresponding Raman spectrum; FESEM images of pure MoSe₂, GCA-MoSe₂-1, and GCA-MoSe₂-3; ECSA evaluation; LSV polarization curves for different GCA-MoSe₂ samples (PDF)

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Notes
The authors declare no competing financial interest.
**Acknowledgments**

The authors are grateful for the financial support from the National Natural Science Foundation of China (51433001, 21674019), China Postdoctoral Science Foundation (2016M601471), Shanghai Sailing Program (17YF1400200), and the Fundamental Research Funds for the Central Universities.

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