Supplementary Information:

Colloidal Synthesized $MoSe_2$/Graphene Hybrid Nanostructures as Efficient Electrocatalysts for Hydrogen Evolution

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Experimental Section

Materials Synthesis

Synthesis of 3D structures assembled from layered $MoSe_2$: A typical procedure is described as follows: a given amount of $(NH_4)_2MoO_4$ (0.5 mmol) and selenium powder (1.0 mmol) was added in 18 mL mixture of oleic acid and ethanol (volume ratio=1:1) in a 20 mL Teflon-lined autoclave. The autoclave was sealed and heated at 160-200 °C for 72 h in an oven, and then cooled down to room temperature. The products were collected by centrifugation and washed several times with ethanol and then dried in a vacuum at 60 °C overnight. To remove the organic residue and excess selenium powder, the as-prepared products were annealed in Ar/H_2 (95%:5%) at 300 °C for 2 h.

Growth of $MoSe_2$ nanoflowers on graphene: GO was made by a modified Hummers method.[S1] Then 20 mg of GO was dispersed in 4 mL of distilled water under constant sonication at room temperature for approximately 60 min until a clear and homogeneous solution was achieved. The following steps were similar to the preparation of $MoSe_2$ except added above mentioned 4 mL of GO solution, the mixed solvents contains 9 mL of oleic acid, 5 mL of ethanol and 4 mL of distilled water. For comparison, the other two $MoSe_2$/rGO hybrid nanostructures with different graphene and $MoSe_2$ ratios were prepared: one is with 0.5 mmol of $(NH_4)_2MoO_4$, 1.0 mol of Se and 10 mg of GO; and the other is with 0.5 mmol of $(NH_4)_2MoO_4$, 1.0 mol of Se and 30 mg of GO.

Characterizations: TEM images were acquired by a Hitachi HT-7700 transmission electron microscope (TEM, Japan) operating at 100 kV. High-resolution TEM (HRTEM) micrographs were obtained with a Philips Tecnai F20 FEG-TEM (The USA) operated at 200 kV. Samples for TEM analysis were prepared by drying a drop of cyclohexane solution containing the nanomaterials on the surface of a carbon-coated copper grid. Raman spectrum of powder samples were recorded on LabRAM HR Raman microscope with a laser excitation wavelength of 532 nm. The X-ray diffraction XRD patterns were obtained using a Rigaku D/MAX-RB with monochromatized Cu Kα radiation (λ=1.5418 Å) in the 2θ ranging from 10° to 80°. Infrared spectra were recorded on a Nicolet 6700 FTIR spectrometer. X-ray photoelectron spectra (XPS) were conducted using a PHI Quantera SXM instrument equipped with an Al X-ray excitation source (1486.6 eV). Binding energies (BEs) are referenced to the C 1s of carbon contaminants at 284.6 eV. All samples were prepared by depositing a thin layer of products onto a cleaned Si wafer and drying at room temperature.

Electrocatalytic measurements for HER: Typically, 4 mg of sample and 30 μL Nafion solution (5 wt%) were dispersed in 1 mL water–ethanol solution with volume ratio of 1:1 by sonicating for 1 h to form a homogeneous ink. Then 5 μL of the dispersion (containing 20 μg of catalyst) was loaded onto a roating disk electrode (RDE) with 3 mm diameter (loading ca. 0.285 mg cm^{-2}). Linear sweep voltammetry with scan rate of 5 mV s^{-1} was conducted in 0.5 M H_2SO_4 (purged with pure N_2) using electrochemical cell setup, with a saturated calomel electrode ($Hg/HgCl_2$ in saturated KCl) as the reference electrode and a Pt wire as the counter electrode, and RDE as the working electrode with a rotating speed of 2000 rpm. All the potentials were converted to values with reference to a reversible hydrogen electrode (RHE). Cyclic voltammetry was conducted at room temperature by using the same standard three-electrode setup ranging from 0.1 to -0.3 V (vs RHE) at a scan rate of 50 mV s^{-1}. Time-dependent current density curve of $MoSe_2$/rGO hybrid nanostructures was conducted under static overpotential of 200 mV for continuous operation of 6000 seconds. Nyquist plots of as-prepared $MoSe_2$ and $MoSe_2$/rGO hybrid were measured at overpotential of 250 mV from 100 kHz to 0.1 Hz with amplitudes of 5 mV.

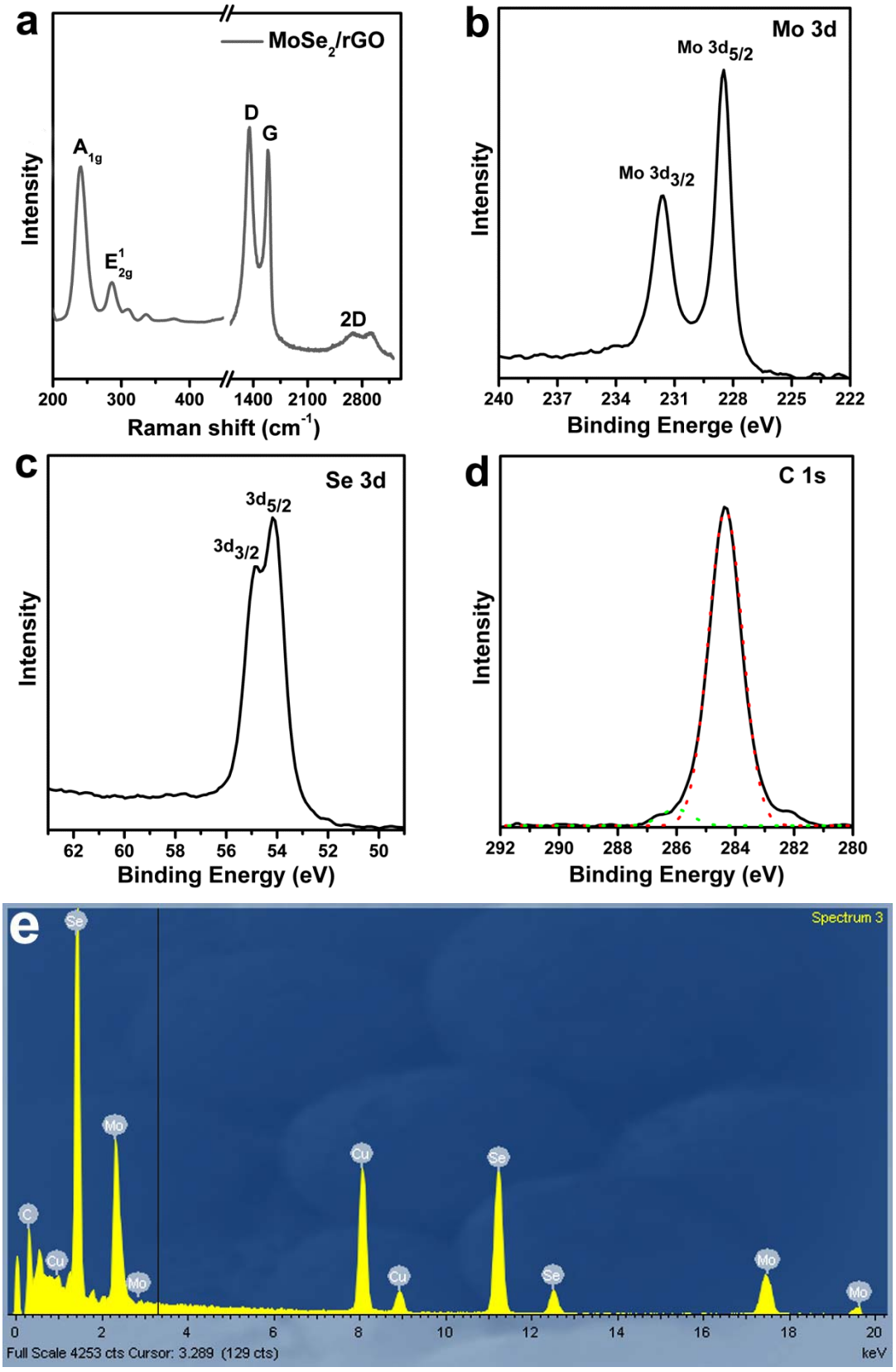

Fig. S1. (a) Raman spectrum and (b-d) XPS spectra of as-obtained $MoSe_2$/rGO hybrid nanostructures. (b) Mo 3d, (c) Se 3d, and (d) C 1s signals recorded for $MoSe_2$/rGO hybrid nanostructures. (e) Energy-dispersive X-ray analysis (EDX) spectrum of $MoSe_2$, note that the Cu signals are from the TEM copper grid substrate.

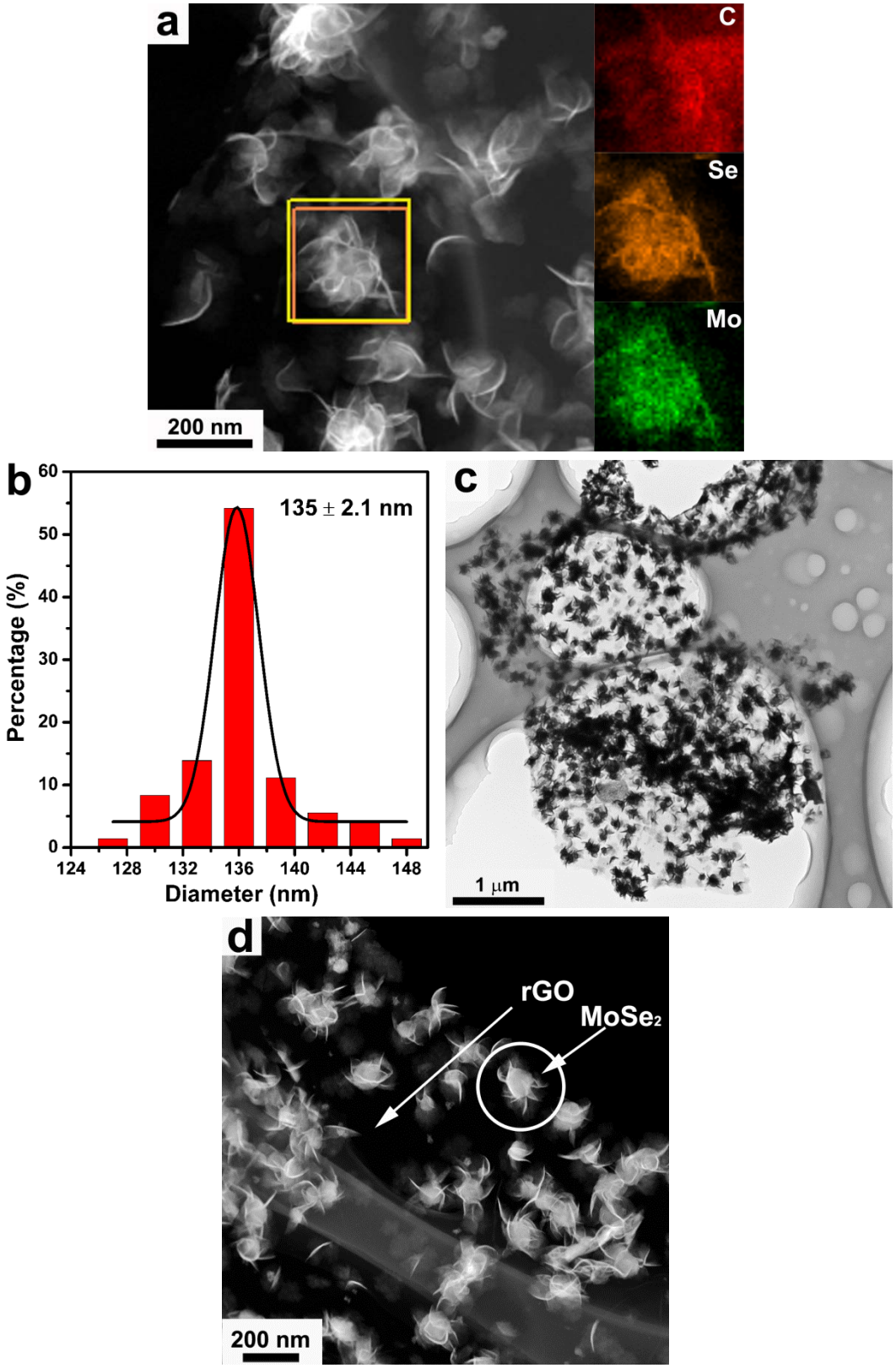

Fig. S2. (a) STEM image and EDX elemental mappings of $MoSe_2$/rGO hybrid. (b) Size distribution histogram showing narrow size distribution of $MoSe_2$ on the graphene surface. (c) 3D $MoSe_2$ nanoflowers grown on graphene in the $MoSe_2$/rGO hybrid nanostructures, with no free $MoSe_2$ nanostructures can be observed. (d) HAADF-STEM image of $MoSe_2$/rGO hybrid nanostructures. From the elemental mapping results, the Mo, Se, and C elements are clearly evidenced in the $MoSe_2$/rGO hybrid, and the distributions and intensities of the signals match well with the $MoSe_2$ nanosheets and rGO structures shown in the STEM image.

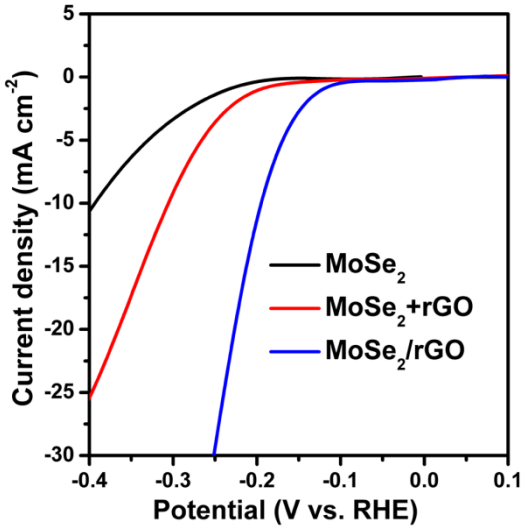

Fig. S3. Polarization curve of $MoSe_2$ nanosheets physically mixed with rGO (0.5 mmol:20 mg), with its performance inferior to $MoSe_2$/rGO hybrid nanostructures.

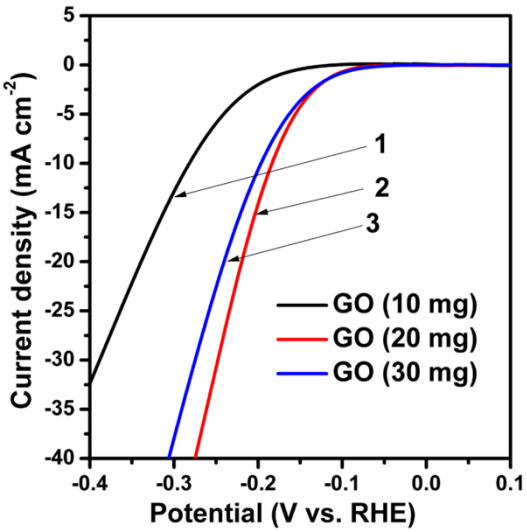

Fig. S4. Polarization curves recorded on glassy carbon electrodes with catalysts of $MoSe_2$/rGO hybrid nanostructures with different ratios. Conditions: loading of 0.285 mg cm^{-2}, potential scan rate of 5 mV s^{-1}, electrode rotating rate of 2000 rpm. The line 1 0.5 mmol $(NH_4)_2MoO_4$, 1.0 mol Se and 10 mg GO, line 2 0.5 mmol $(NH_4)_2MoO_4$, 1.0 mol Se and 20 mg GO, and line 3 0.5 mmol $(NH_4)_2MoO_4$, 1.0 mol Se and 30 mg GO.

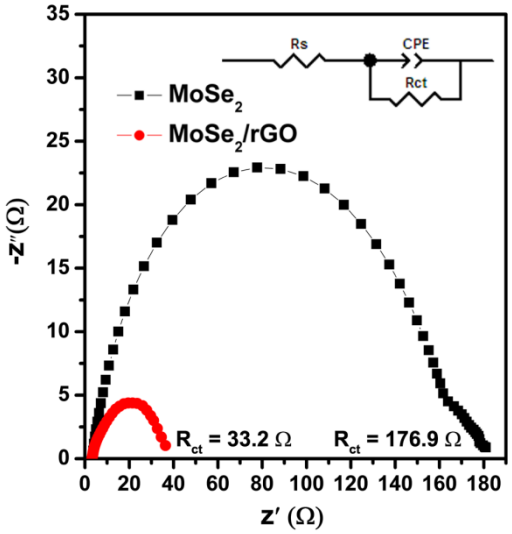

Fig. S5. Nyquist plots of the $MoSe_2$ and $MoSe_2$/rGO hybrid nanostructures, showing the imaginary part versus the real part of impedance. The $MoSe_2$/rGO hybrid only showed a charge transfer resistance (R_{ct}) of around 33.2 Ω, which is much smaller than R_{ct} of $MoSe_2$ nanosheets (176.9 Ω). This also demonstrates that the rGO can dramatically enhance the electron transfer.

Reference:

[S1] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, J. M. Tour, *ACS Nano* 2010, **4**, 4806.