Efficient and sustainable hydrogen evolution reaction: Enhanced Photoelectrochemical Performance of ReO$_3$-incorporated Cu$_2$Te Catalysts

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2 Experimental methods

2.1 Material characterization

The morphology and elemental composition of the samples were analyzed using Scanning electron microscopy(SEM) using FESEM Hitachi S46600. XRD patterns were recorded with PANalytical X'Pert^3 powder X-ray diffractometer with CuKα radiation having excitation wavelength 1.5406 A$^\circ$. Raman analysis was carried out at room temperature using Horiba LabRAM HR Evolution Confocal Raman spectrometer with a 532nm laser wavelength. Elemental species and associated chemical state were confirmed by survey and high-resolution XPS spectra obtained from PHI versaprobe III. Ocean Optics fiber optic spectrometer was used for taking UV-Vis diffuse reflectance spectroscopy with BaSO$_4$ as the reflectance standard.

2.2 Electrochemical measurements

The electrochemical performance of the synthesized catalysts were measured using CHI760E electrochemical workstation. The analysis was performed in a three-electrode set up at room temperature in 0.5 M H$_2$SO$_4$ under an inert atmosphere. The catalysts deposited copper foam (CF) and were used as the working electrode, Ag/AgCl, and graphite were used as the reference electrode and counter electrode. All the measured potential values using Ag/AgCl reference electrode were calibrated with respect to the reversible hydrogen

electrode (RHE). Calibration measurements were performed in a three-electrode setup was used with platinum and Ag/AgCl as working and counter electrodes. Prior to the experiment, the 0.5M sulfuric acid electrolyte was saturated with high-purity hydrogen for 30min. Cyclic voltammetry (CV) was performed at a scan rate of 0.1V/sec. From the CV data, the thermodynamic potential for the hydrogen electrode reaction was determined from the average of the two potentials at which the current crossed zero. The CV curve obtained is shown in Figure S.1, and the calibration value is obtained as 0.209V. So all the potentials are converted to RHE using the equation,
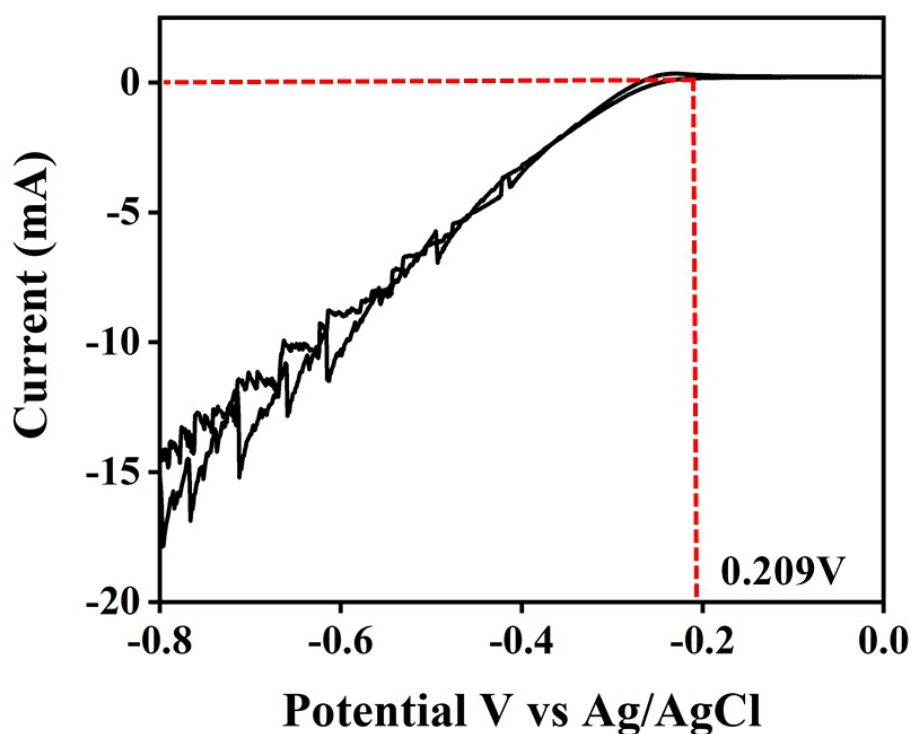
$$VRHE = VAg/AgCl + 0.209$$

Figure S.1 CV curve for Ag/AgCl electrode calibration in 0.5M H_2SO_4

Copper foam was cut into 1x2 cm^2 dimensions to prepare the working electrodes. Cleaning of CF was conducted using 15min ultrasonication in acetone followed by 2min ultrasonication in DI water twice. Deposition of the catalysts were done using CVD synthesis as described in the manuscript in session 2.2. The linear sweep voltammetry technique has been

used to identify the electrochemical HER performance of the catalyst. Further, to analyze the stability of the catalyst, chronoamperometry was performed. Linear sweep voltammetry has been recorded at a scan rate of 50mV/sec in the potential range -0.8V to 0.2V vs RHE in 0.5M H_2SO_4 solution. Every LSV measurement was recorded after 25 CV cycles to activate the catalyst surface. Chrono amperometry was performed for 20000 sec in 0.5M H_2SO_4 solution at a constant potential -0.3V.

2.3 Photoelectrochemical measurements

Photoelectrochemical performance towards HER was measured with CHI760E electrochemical workstation at room temperature. Three-electrode set up with 0.5M H_2SO_4 solution as the electrolyte was used for analysis and 250W halogen lamp as the irradiation source. The catalysts deposited copper foam (CF), graphite electrode, and Ag/AgCl electrode was used as working, counter, and reference electrodes, respectively. For the preparation of the working electrodes, copper foam was cut into 1x2 cm^2 dimensions. Cleaning of CF was conducted using 15min ultrasonication in acetone followed by 2min ultrasonication in DI water twice. Deposition of catalyst were done using CVD synthesis as described in the manuscript in session 2.2. Linear sweep voltammetry, electrochemical impedance spectroscopy, chronoamperometry, and Mott-Schottky analyses were carried out to analyze the photoelectrochemical performance of the catalyst. Linear sweep voltammetry has been recorded at a scan rate of 50mV/sec in the potential range -0.8V to 0.2V vs RHE under dark and light conditions. Chronoamperometry was performed at a constant potential of -0.6V. EIS measurements were carried out at a potential -0.6V from a high frequency of 10^5Hz to a low frequency of 0.08Hz.

3.2 Chemical characterization

To identify in which form the rhenium got incorporated in the samples, ammonium perrhenate alone is treated under the same synthesis condition. The XRD analysis of the sample suggests

the formation of rhombohedral ReO_3 (00-045-1039) along with traces of monoclinic ReO_2 (00-017-0600), as shown in Figure S.2.

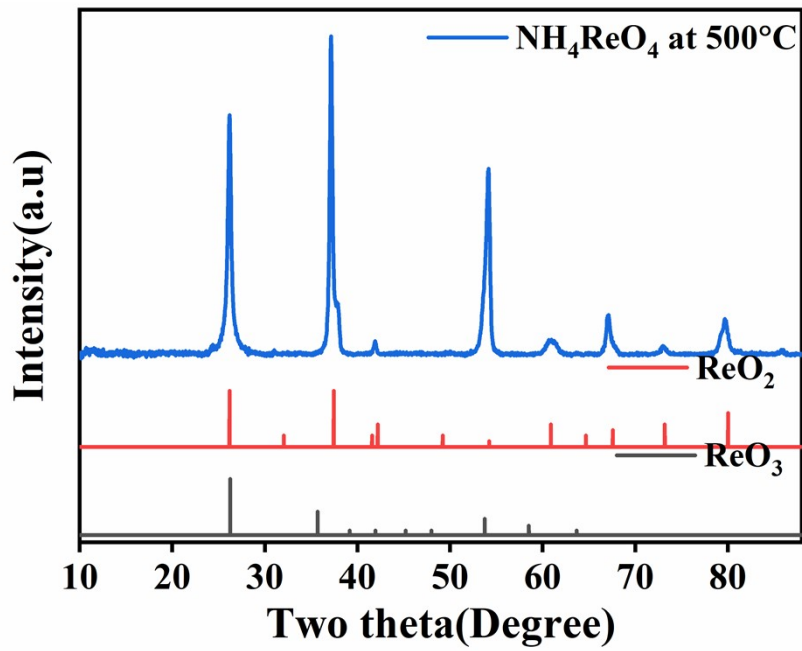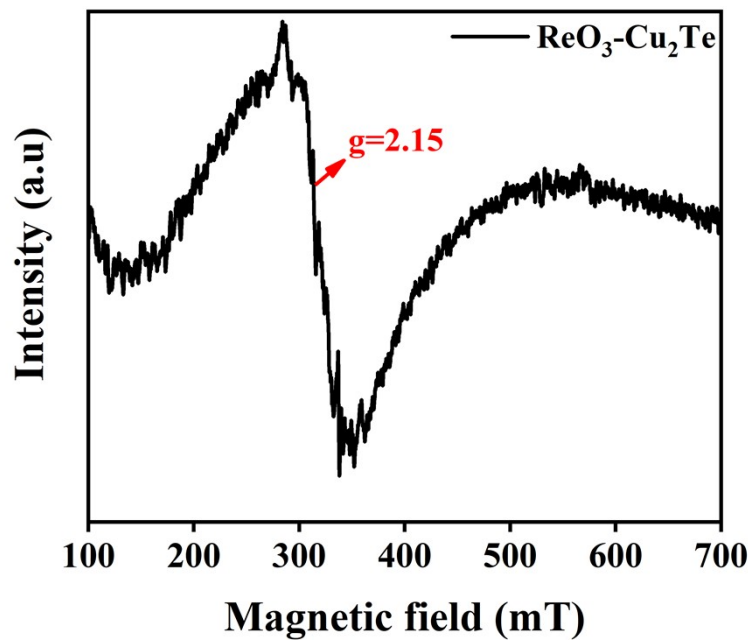Figure S.2 XRD pattern of.the material after heating NH_4ReO_4 at 500°C indicating the formation of ReO_3 and ReO_2

Figure S.3 EPR spectrum of ReO_3-Cu_2Te

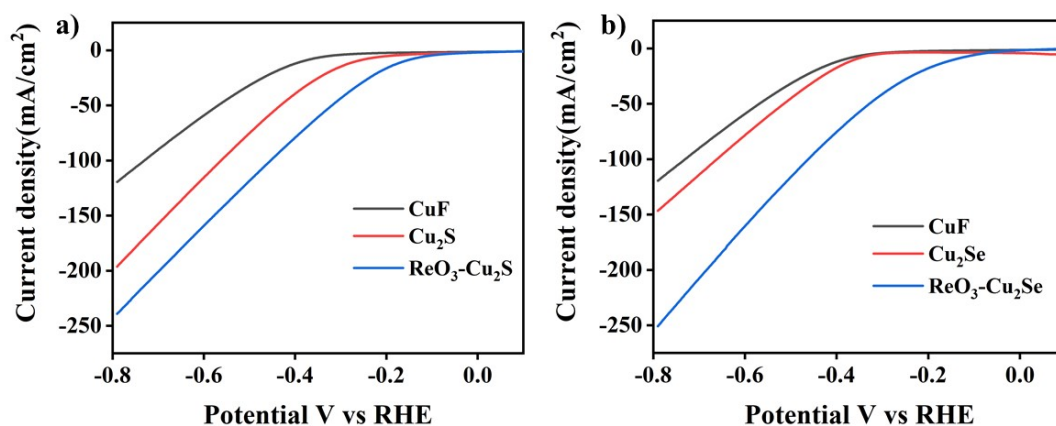## 3.3 Electrochemical hydrogen evolution reaction

Figure S.4 (a) Polarisation curve of CuF, Cu_2S, ReO_3-Cu_2S (b) CuF, Cu_2Se, ReO_3-Cu_2Se.

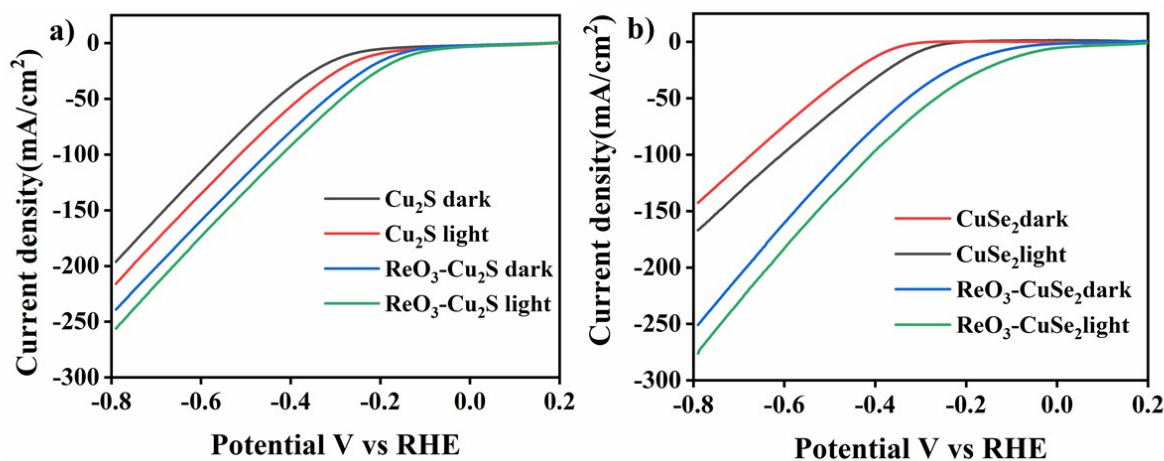## 3.5 Photoelectrochemical hydrogen evolution reaction

Figure S.5 (a) Polarisation curve of Cu_2S, ReO_3-Cu_2S (b) Cu_2Se, ReO_3-Cu_2Se

The fitted circuit parameter values were given in Table S1 .

Parameter	Cu_2Te dark	Cu_2Te light	ReO_3-Cu_2Te dark	ReO_3-Cu_2Te light
R1(Ω)	2.58	2.21	1.58	1.73
Q1 (F.s^(a-1))	0.06	5.15e-3	0.02	0.01
n	0.98	0.81	0.62	0.73

R2(Ω)	-0.74e-3	15.08	-8.45e-3	1.28
C3(F)	-0.05	2.52e-3	-0.43e-3	0.01
R3(Ω)	102.80	33.93	8.89	1.27

Table S.1. Nyquist circuit element values for Cu_2Te and ReO_3-Cu_2Te in dark condition and under simulated solar light irradiation after fitting the circuit

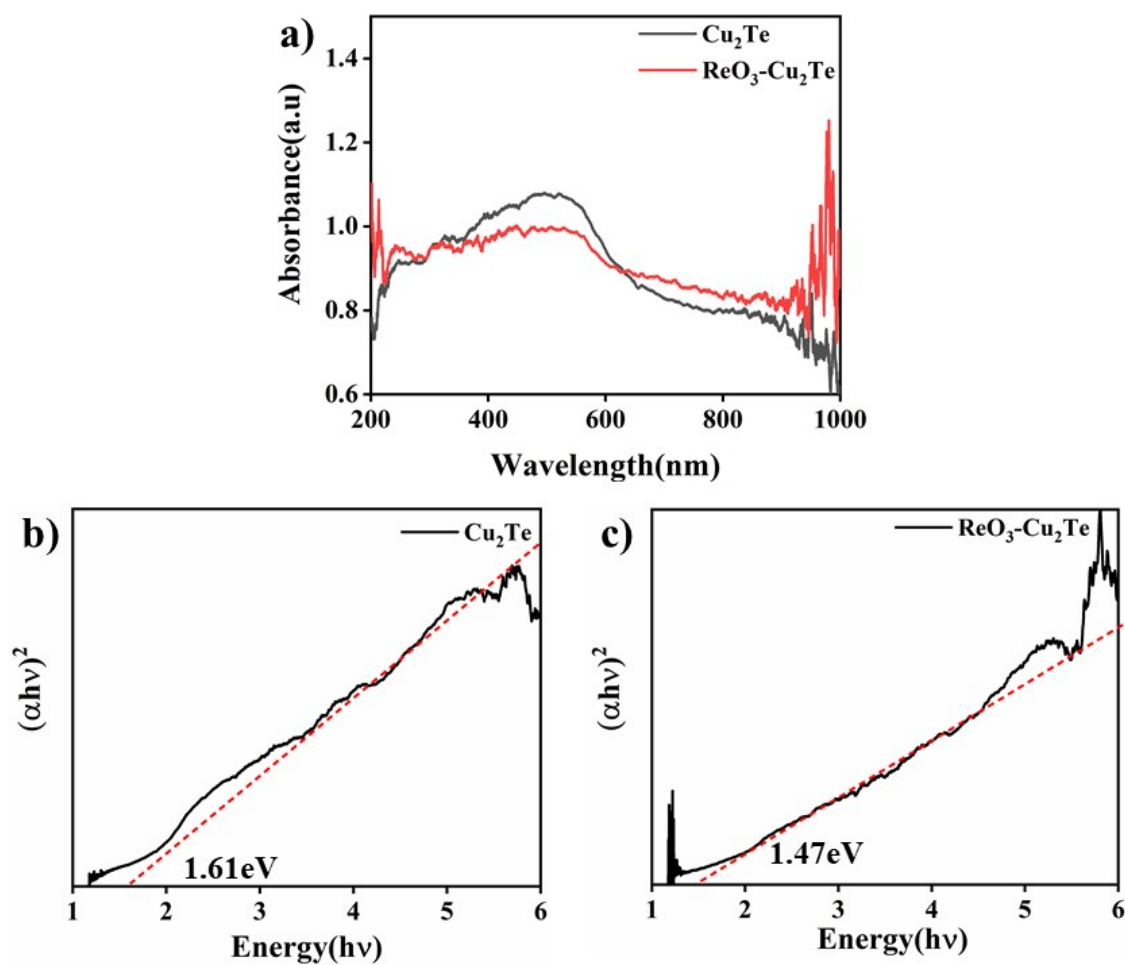Figure S.6 UV-Vis absorption spectra of (a) Cu_2Te, ReO_3-Cu_2Te and Tauc plot of (b) Cu_2Te (c) ReO_3-Cu_2Te.