Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.


**SUPPLEMENTARY MATERIAL**

# Ru-based nanoparticles supported on carbon nanotubes for electrocatalytic hydrogen evolution: structural and electronic effects

Nuria Romero,[a,b*,&] Dídac A. Fenoll,[a,&] Laia Gil,[a] Sergi Campos,[a] Jordi Creus,[a,b] Gerard Martí,[a] Javier Heras-Domingo,[a] Vincent Collière,[b] Camilo A. Mesa,[c] Sixto Giménez,[c] Laia Francàs,[a] Luis Rodríguez-Santiago,[a] Xavier Solans-Monfort,[a*] Mariona Sodupe,[a] Roger Bofill,[a] Karine Philippot,[b*] Jordi García-Antón,[a] and Xavier Sala[a*]

[a] Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra (Cerdanyola del Vallès), Catalonia (Spain). E-mail: xavier.sala@uab.cat, xavier.solans@uab.cat

[b] CNRS, LCC (Laboratoire de Chimie de Coordination), UPR8241, Université de Toulouse, UPS, INPT, F-31077 Toulouse cedex 4, France. E-mail: nuria.romero@lcc-toulouse.fr, karine.philippot@lcc-toulouse.fr

[c] Institute of Advanced Materials (INAM), Universitat Jaume I, Avenida de Vicente Sos Baynat, s/n, 12006 12006 Castelló de la Plana, Castellón, Spain.

* Corresponding authors

& These authors contributed equally to this work.

**List of Contents** **page**

# 1. Electron microscopy characterization of the hybrid nanomaterials

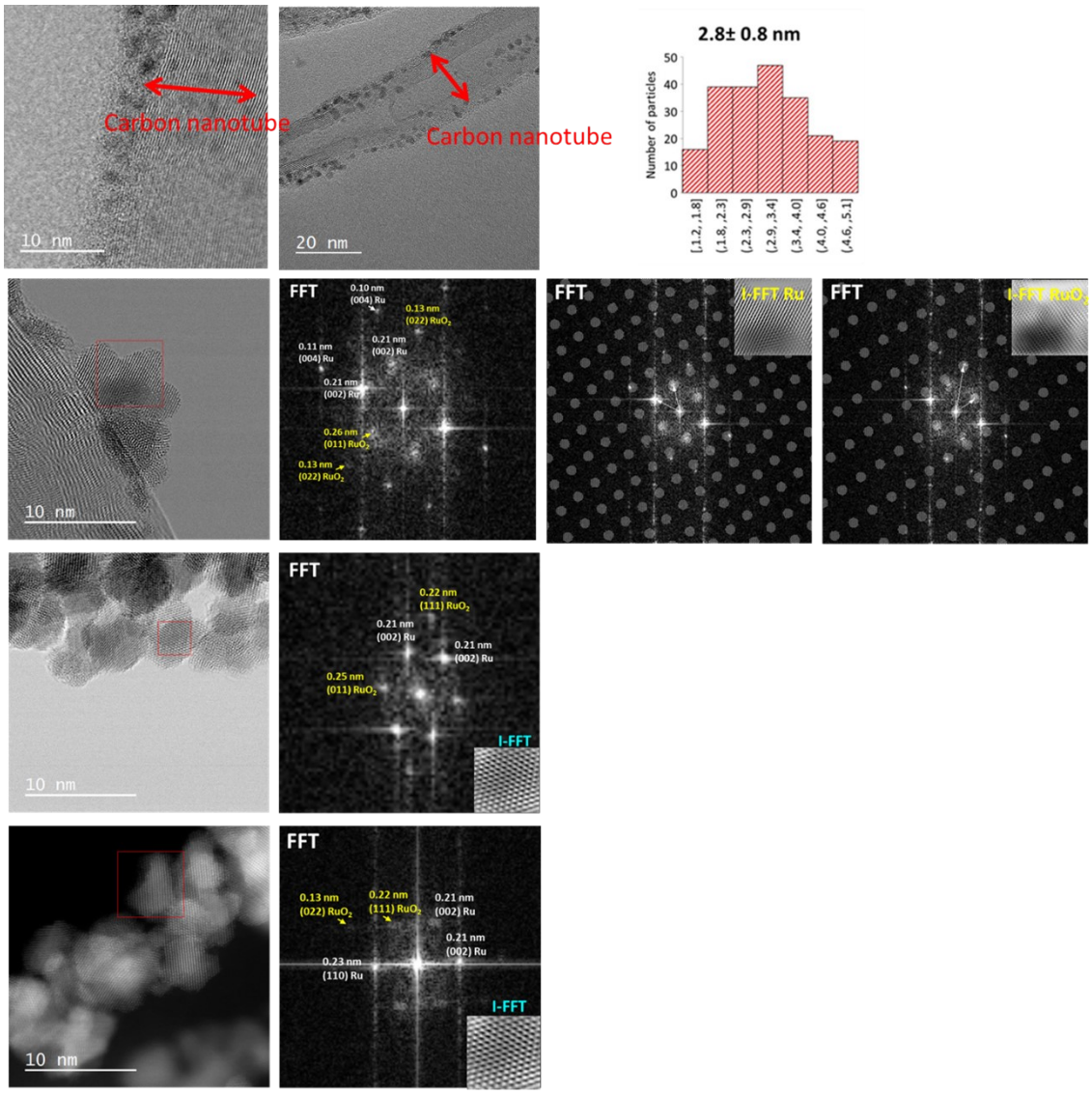


**Figure S1**. HRTEM images and size histogram of the **Ru@$RuO_2$/CNT** nanomaterial, including electron diffraction patterns after Fast Fourier Transform treatment of individual nanoparticles (on a holy carbon covered Cu grid).

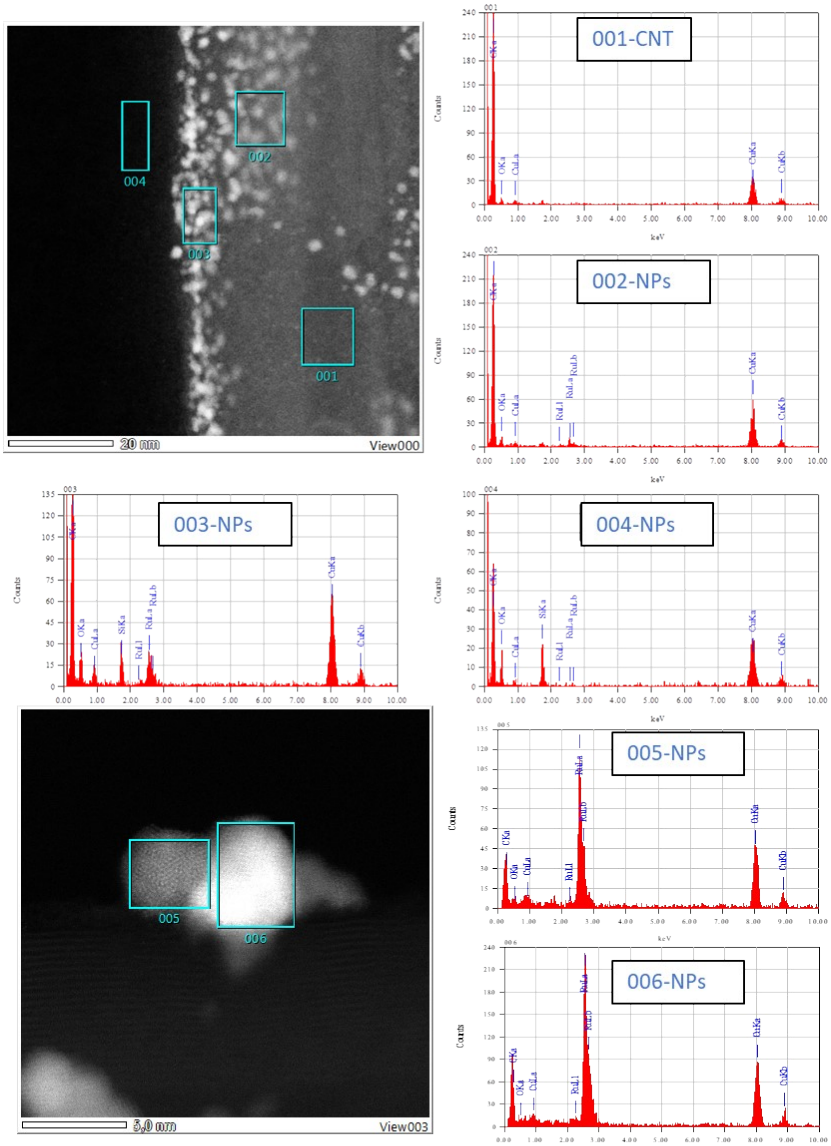


**Figure S2.** EDX spectra on different regions of HRTEM images of **Ru@RuO$_2$/CNT**: general EDX analysis (top) and nanoparticle analysis (bottom, holy carbon covered Cu grid).

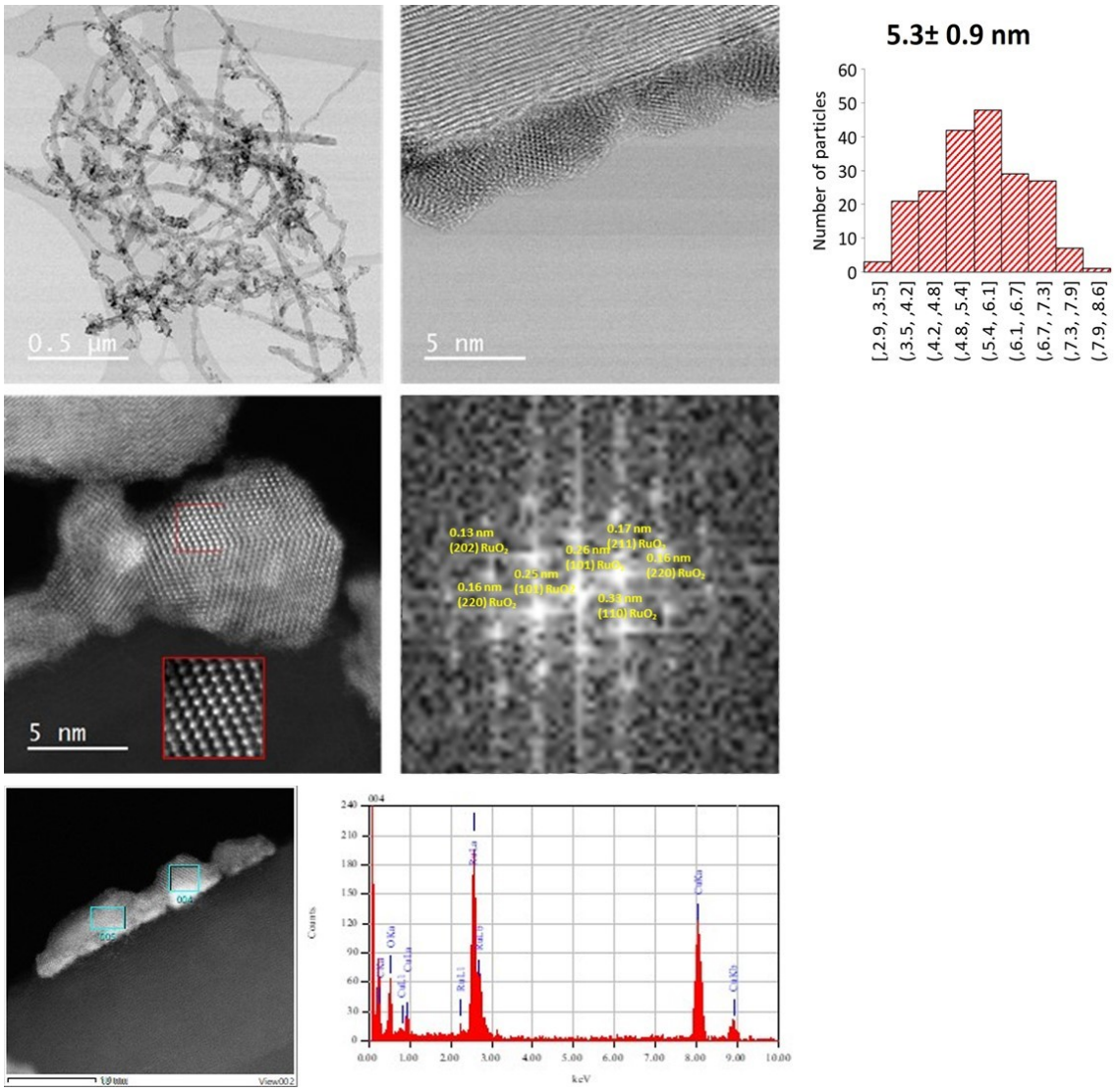


**Figure S3.** TEM and HRTEM images, NPs size histogram, FFT pattern and EDX analysis of the **$RuO_2$-10'/CNT** nanomaterial.

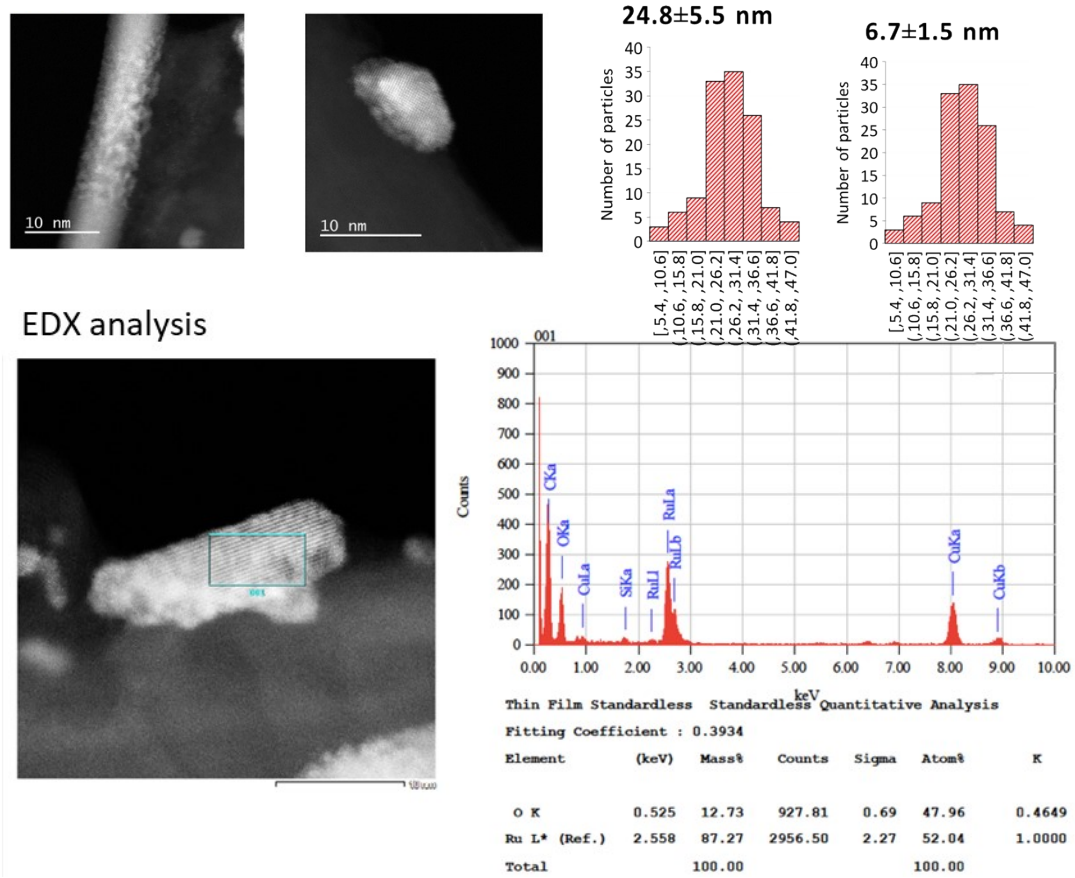


**Figure S4.** TEM and HRTEM images, NPs size histogram and EDX analysis of the **$RuO_2$-120'/CNT** nanomaterial.

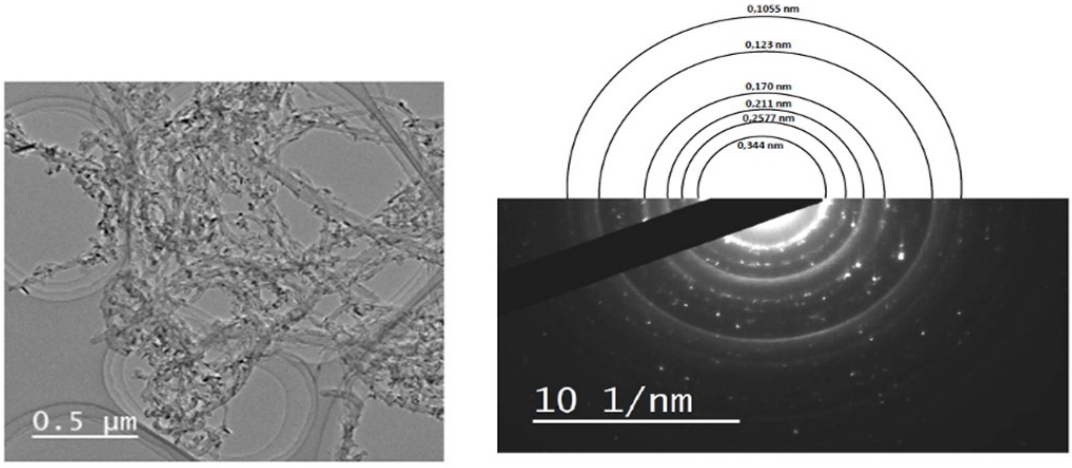


**Figure S5.** Electron diffraction analysis of a large zone of the **$RuO_2$-120'/CNT** nanomaterial.

## 2. HER catalytic studies of the hybrid nanomaterials

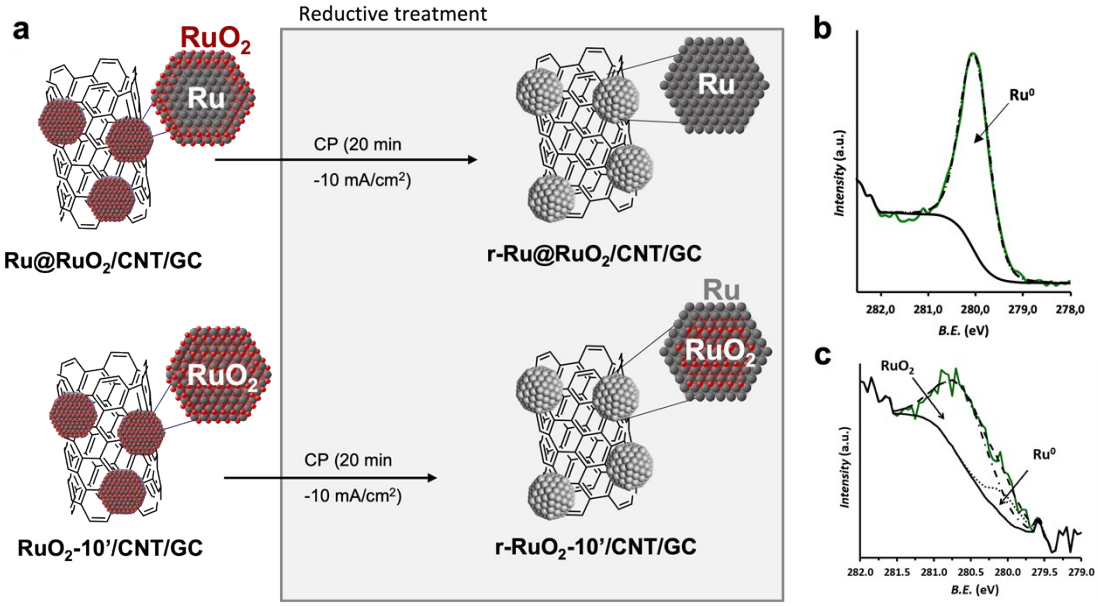


**Figure S6.** (a) Scheme of the chronopotentiometry reductive treatment applied to the GC RDE deposited nanomaterials, leading to their reduced counterparts. (b) XPS spectrum of **r-Ru@$RuO_2$/CNT/GC** and (c) XPS spectrum of **r-$RuO_2$-10'/CNT/GC**. The $RuO_2$ component is shown in dotted-dashed black, the Ru(0) component in dotted black, the envelope in dashed black, the experimental data in solid green and the background signal in solid black.

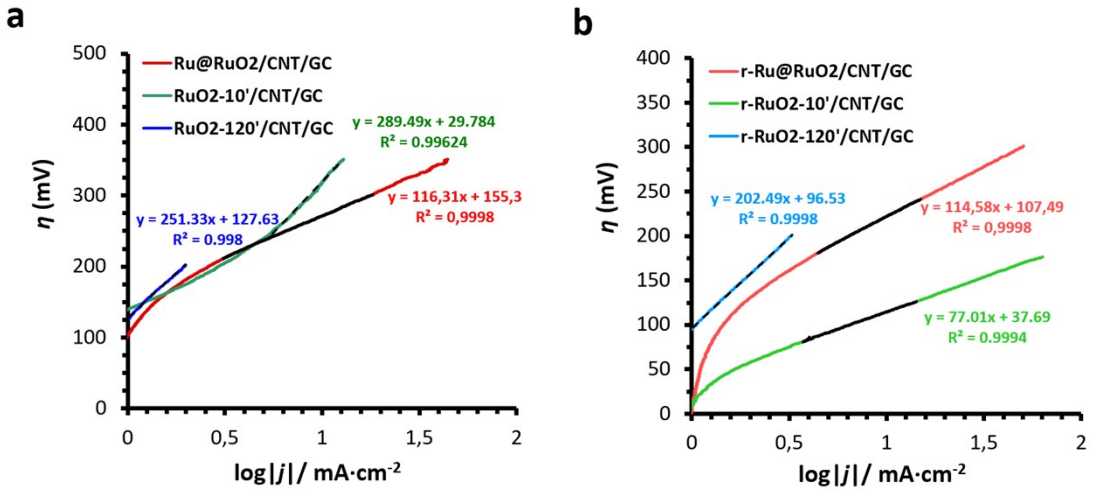


**Figure S7.** Tafel plots in 1 M $H_2SO_4$ corresponding to the HER process of **Ru@$RuO_2$/CNT/GC** (red), **$RuO_2$-10'@CNT/GC** (green) and **$RuO_2$-120'/CNT/GC** (blue) (a), and of their reduced counterparts, **r-Ru@$RuO_2$/CNT/GC** (orange), **r-$RuO_2$-10'/CNT/GC** (light green) and **r-$RuO_2$-120'/CNT/GC** (light blue) after a 20 min reductive chronopotentiometry at $j$ = -10 mA·cm$^{-2}$ (b).

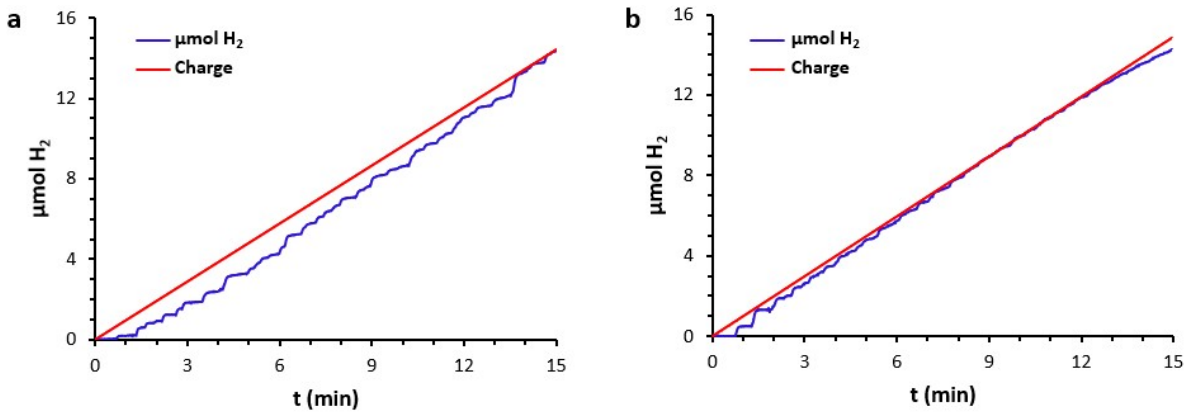


**Figure S8.** $H_2$ measurement during a reductive CP at -10 mA·cm$^{-2}$ for **r-Ru@RuO$_2$/CNT/FTO** (a), and **r-RuO$_2$-10'/CNT/FTO**, (b), in 1 M $H_2SO_4$.

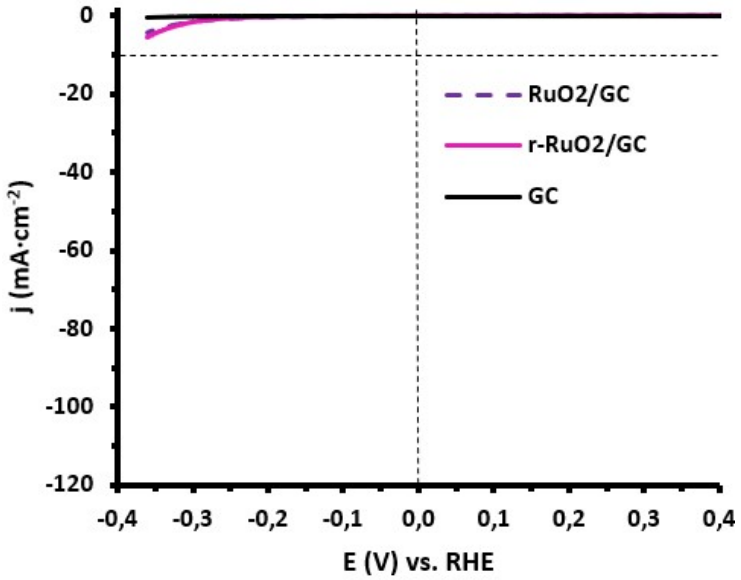


**Figure S9**. LSVs in 1 M $H_2SO_4$ of bulk commercial **RuO$_2$/GC** (dashed purple), **r-RuO$_2$/GC** (solid pink) and the bare GC electrode (solid black). The thermodynamic HER potential in 1 M $H_2SO_4$ and the reference j = -10 mA·cm$^{-2}$ current density are indicated as black dashed lines.

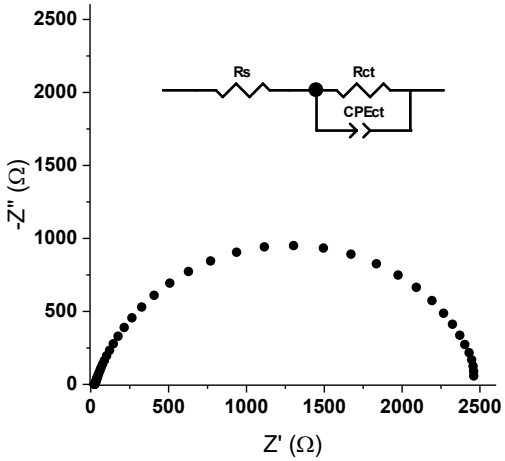


**Figure S10.** Typical Nyquist obtained for the electrodes studied herein. Nyquist plot of **CNT/GC** measured at -0.3 V vs NHE. Inset: Randles circuit employed to fit the experimental data.

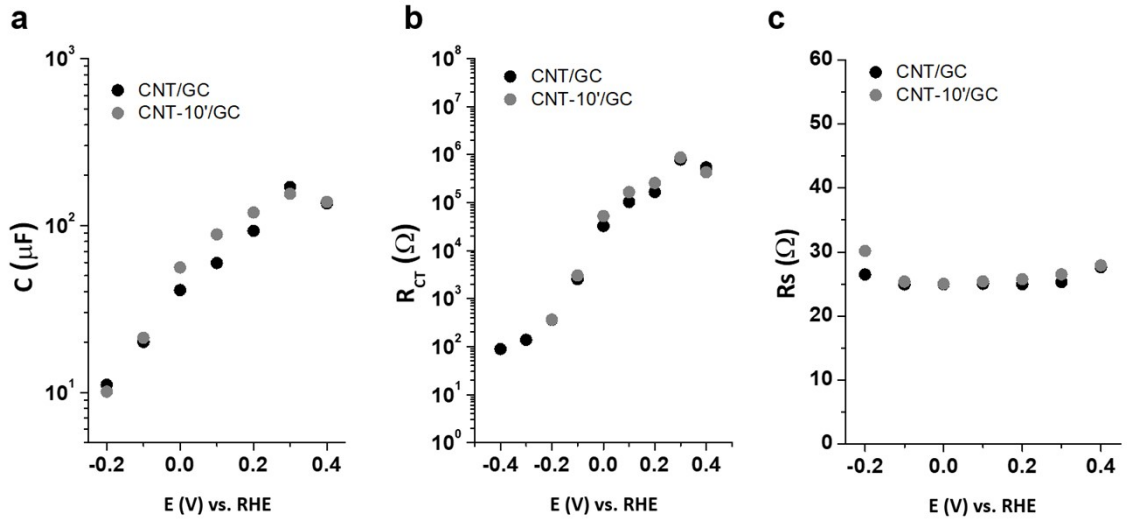


**Figure S11.** Impedance spectroscopy results C, R1 and Rs, fitting the Nyquist plots to a simple Randles circuit of **CNT/GC** (black) and **CNT-10'/GC** (dark grey). (a) Capacitance (C), (b) charge transfer resistance ($R_{CT}$) and (c) series resistance (Rs).

**Table S1.** Main physicochemical and electrochemical data of the CNT-supported Ru-based nanomaterials for HER in 1 M $H_2SO_4$.

| ***Entry*** | ***System*** | ***NP mean size* (nm)** | ***NP composition*** | $\eta_0$ **(mV)** | $\eta_{10}$ **(mV)** | ***b*** **(mV·dec$^{-1}$)** |
|---|---|---|---|---|---|---|
| *1* | **Ru@$RuO_2$/CNT/GC** | 2.8 ± 0.8 | $Ru^0/RuO_2$ core/shell | 200 | 272 | 116 |
| *2* | **r-Ru@$RuO_2$/CNT/GC** [i] | --- | $Ru^0$ [ii] | 150 | 222 | 115 |
| *3* | **$RuO_2$-10'/CNT/GC** | 5.3 ± 0.9 | $RuO_2$ | 130 | 319 | 289 |
| *4* | **r-$RuO_2$-10'/CNT-/GC**[i] | --- | $RuO_2/Ru^0$ core/shell | 50 | 115 | 77 |
| *5* | **$RuO_2$-120'/CNT/GC** | Nanorods: broad (6.7 ± 1.5 nm) and long (24.8 ± 5.5 m) crystals | $RuO_2$ | 125 | - | 251 |
| *6* | **r-$RuO_2$-120'/CNT/GC** [i] | --- | $RuO_2$ | 95 | - | 202 |

[i] *These nanomaterials were treated under chronopotentiometry reductive conditions (j = -10 mA·cm$^{-2}$) for 20 min.* [ii] *The oxidation state is assumed on the basis of literature data (ref. 5*).

## 3. Computational studies

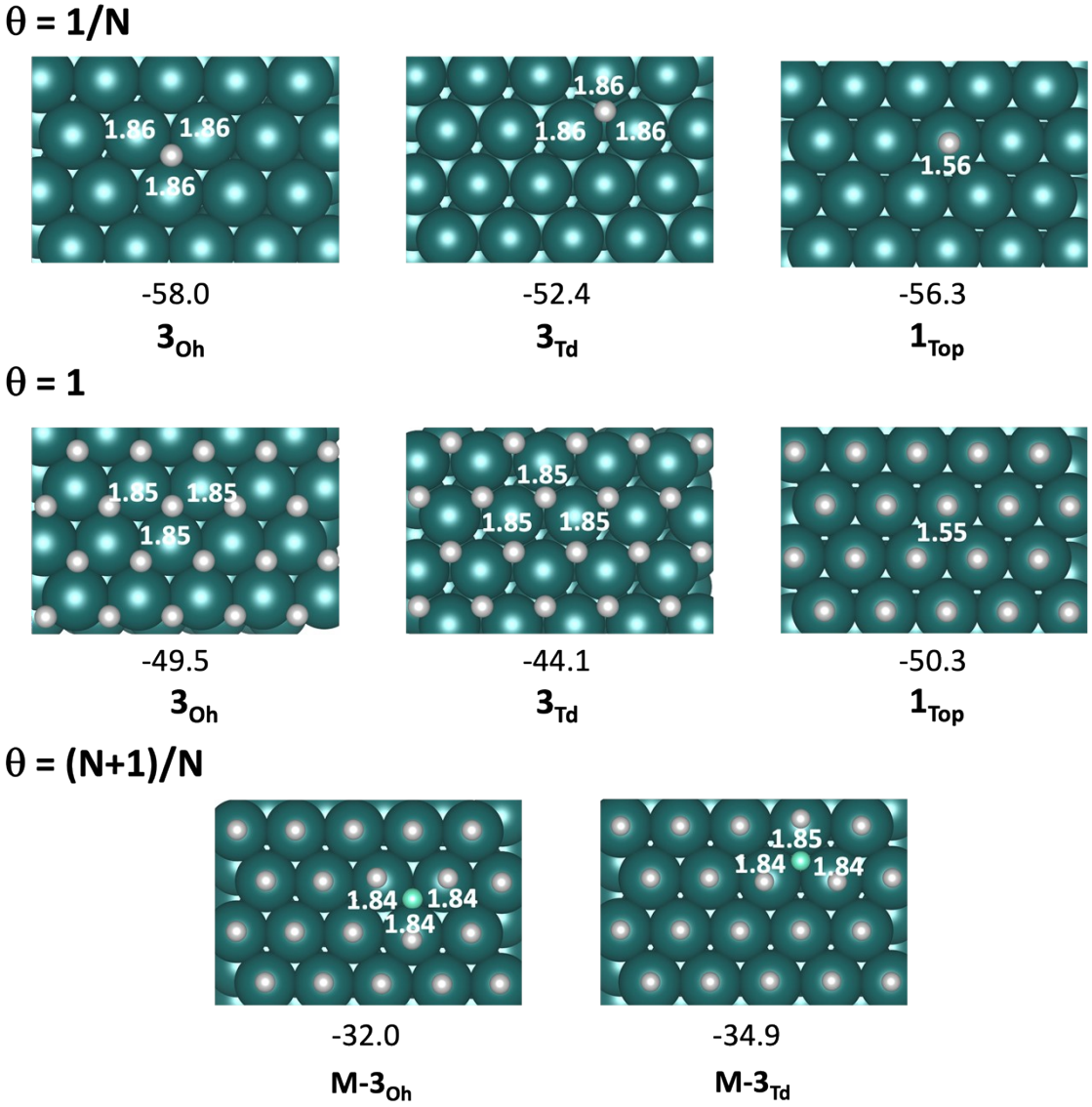


**Figure S12.** Optimized structures and adsorption energies for hydrogen onto a **Pt** surface as a function of the coverage. The additional hydrogen in the θ = 1 coverage is represented in pale green. Pt-H distances are in Å and energies in kJ·mol$^{-1}$.

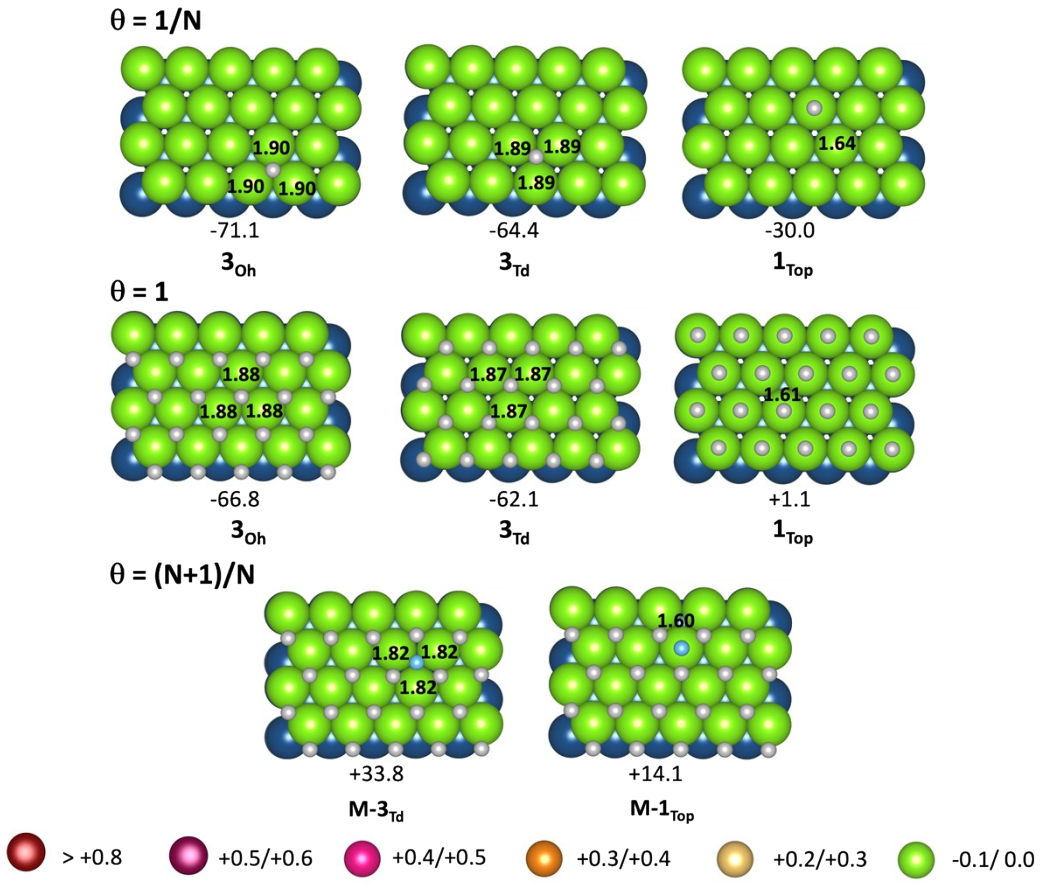


**Figure S13.** Optimized structures and adsorption energies for hydrogen onto a **Ru** surface as a function of the coverage. The additional hydrogen in the θ = 1 coverage is represented in pale blue. The outermost atom color labeling indicates the atomic Bader charges of the pristine material. Ru-H distances are in Å and energies in $kJ \cdot mol^{-1}$.

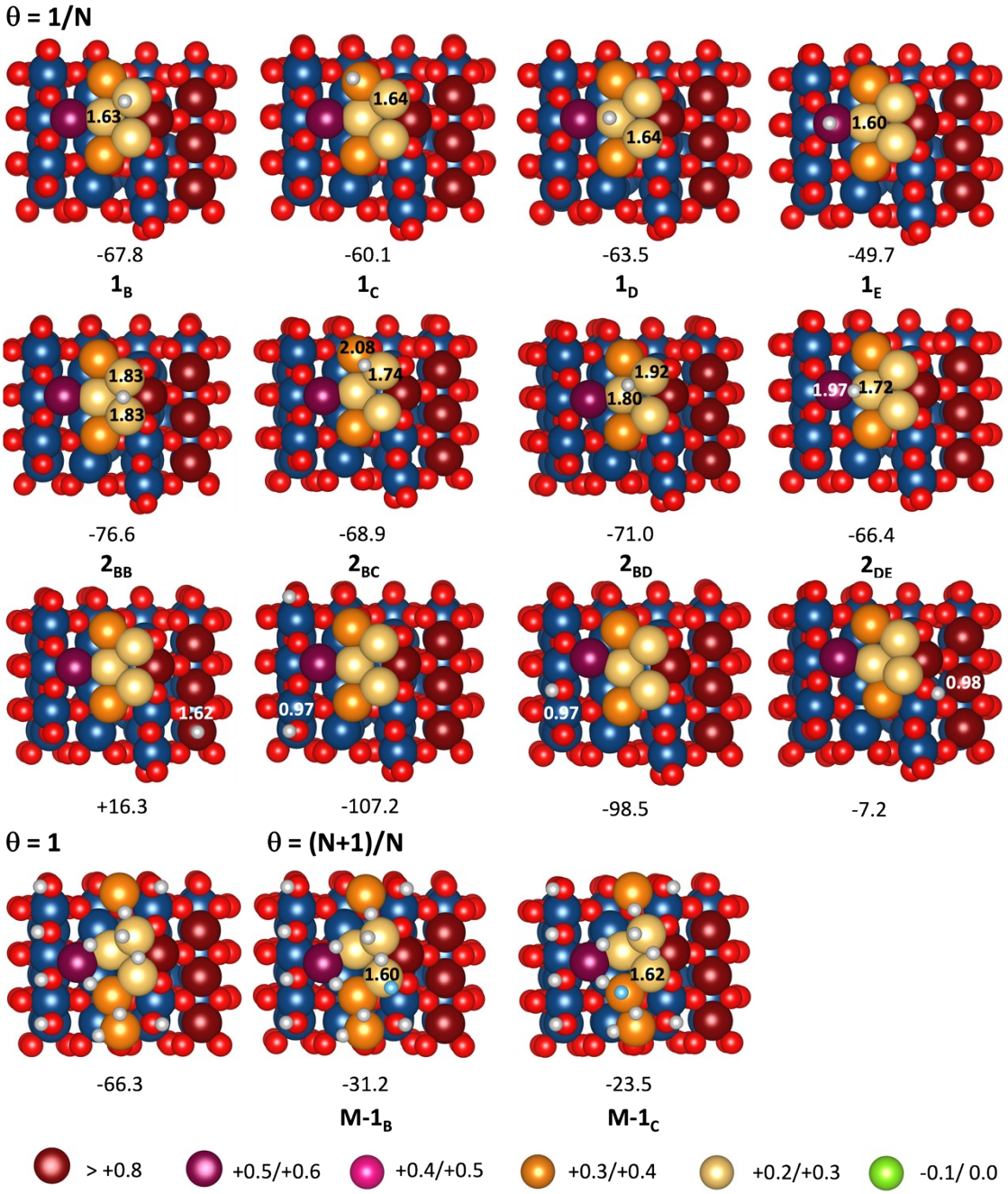


**Figure S14.** Optimized structures and adsorption energies for hydrogen onto a **$RuO_2$@$Ru_7$** model of **r-$RuO_2$-10'/CNT/GC** as a function of the coverage. The additional hydrogen in the θ = 1 coverage is represented in pale blue. The outermost atom color labeling indicates the atomic Bader charges of the pristine material. Ru-H distances are in Å and energies in kJ·mol$^{-1}$.

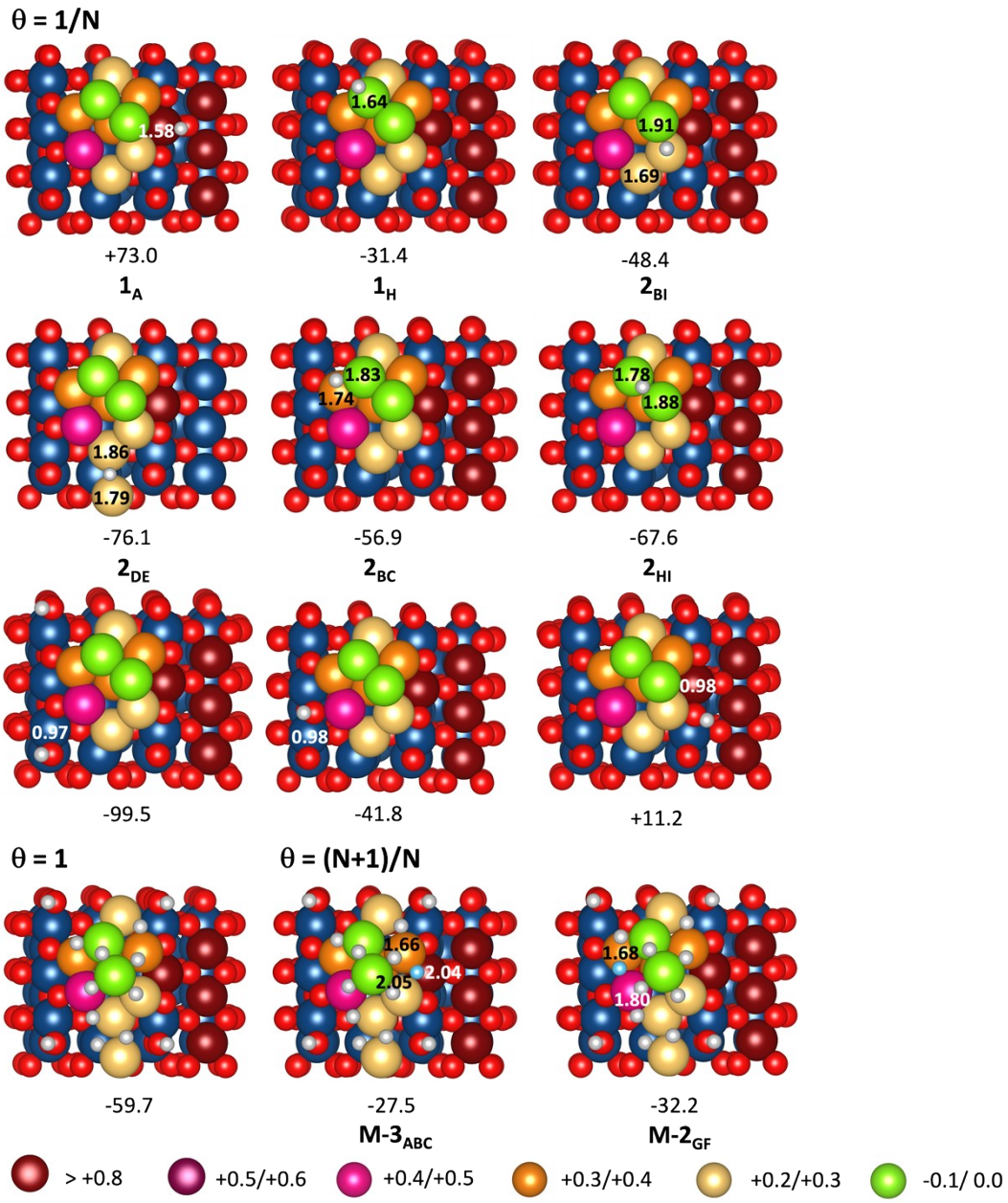


**Figure S15.** Optimized structures and adsorption energies for hydrogen onto a **$RuO_2$@$Ru_{10}$** model of **r-$RuO_2$-10'/CNT/GC** as a function of the coverage. The additional hydrogen in the θ = 1 coverage is represented in pale blue. The outermost atom color labeling indicates the atomic Bader charges of the pristine material. Ru-H distances are in Å and energies in kJ·mol$^{-1}$.

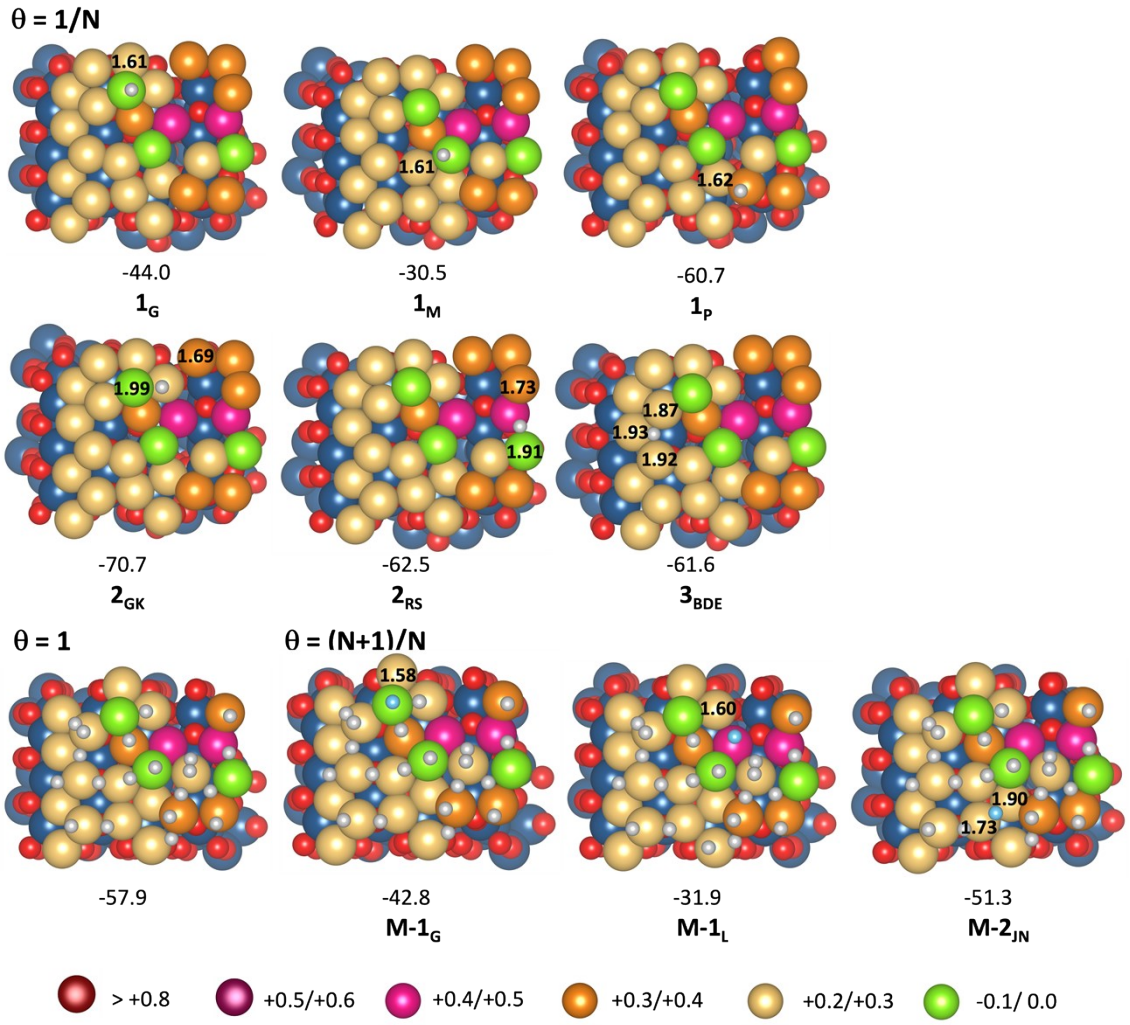


**Figure S16.** Optimized structures and adsorption energies for hydrogen onto a **$RuO_2$@$Ru_{20}$** model of **r-$RuO_2$-10'/CNT/GC** as a function of the coverage. The additional hydrogen in the θ = 1 coverage is represented in pale blue. The outermost atom color labeling indicates the atomic Bader charges of the pristine material. Ru-H distances are in Å and energies in kJ·mol$^{-1}$.

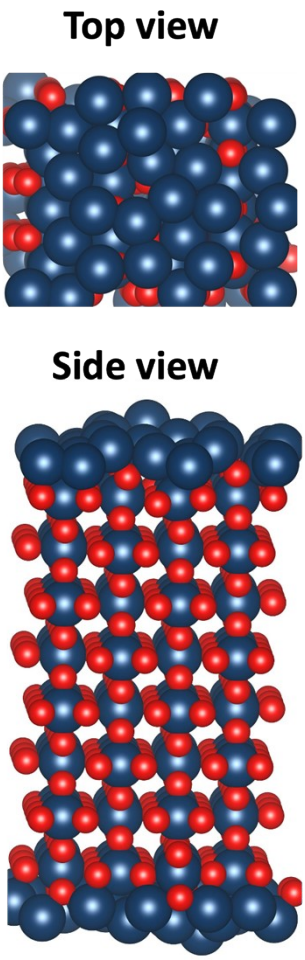


**Figure S17.** $RuO_2$@$Ru_{20}$ model including eight $RuO_2$ layers in the core.