Thermal and light irradiation effect on the electrocatalytic performance of hemoglobin modified Co₃O₄-g-C₃N₄ nanomaterials for oxygen evolution reaction

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Synthesis of Ruthenium Oxide Nanoparticles (RuO₂ NPs) by precipitation method.^{S1,S2}

 RuO_2 NPs were synthesized according the protocol described previously with slightly modifications. Briefly, 0.28 g of $RuCl_3 H_2O$ were solved into 15 mL of ultrapure water and, subsequently, 2 mL of propionic acid was added as pro-surfactant. Then, under vigorous stirring, 15 mL of NaOH 1.5 M were added dropwise to the mixture, increasing the pH up to 9. Next, the resulting reaction mixture was heated at 80 °C for 1h. After that, the formed product was the product formed was separated by centrifugation at 7500 rpm for 20 min. The resulting pellet was suspended in ultrapure water (or ethanol) and then centrifugated again. This purification process was repeated at least 3 times. After that, the purified pellet was dried overnight at 60 °C and lastly calcinated at 900 °C for 4 hours.

X-Ray Diffraction (XRD) measurements confirmed the successful synthesis of RuO_2 NPs (Fig. S1), showing the characteristic XRD pattern for this type of electrocatalyst material (observed plan diffractions: 110, 101, 200, 211, 220, 002, 310, 112, 301).^{S1,S3}



Fig. S1 XRD pattern of the resulting RuO_2 NPs, indicating the characteristic Miller indices (JCPDS Card Number 21-1172) with a main diffraction peak at 28° of the (110) plane.



Fig. S2 XPS spectra of (A-D) 10%Co/g-C₃N₄ and (E-H) 10%Co/g-C₃N₄-Hb samples.



Fig. S3 SEM-mapping images of (A-E) 10%Co/g-C₃N₄ and (F-K) 10%Co/g-C₃N₄-Hb samples. Scale bar: 500 nm.

Determining the number of active sites by Cyclic Voltammetry.^{\$4,\$5}

A sequence of cyclic voltammetries (CVs) were performed in a narrow potential window of -0.717 to -0.817 vs RHE (i.e. where no faradaic reactions occurred) at different scan rates (12-48 mV·s⁻¹ at an interval of 4 mV·s⁻¹). Sequentially, the slope (i.e. areal capacitance) of the lines obtained through the plotting of the J_{anodic}-J_{cathodic} (at -0.767 V vs RHE) against the scan rate was used to determine the number of active sites as well as the electrochemical surface area of each sample.



Fig. S4 Plots of the resulting anodic and cathodic current densities against the scan rate for the more representative samples that is proportional to the number of active sites.



Fig. S5 XPS spectra of 10%Co/g-C₃N₄ and 10%Co/g-C₃N₄-Hb based electrodes before and after the reaction.

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