Supplementary Materials: {Ni_4O_4} Cluster Complex to Enhance the Reductive Photocurrent Response on Silicon Nanowire Photocathodes

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Photocurrent and GC measurements:

Photocurrent experiments were performed using an Abet solar simulator (air mass 1.5–1 sun) and calibrated against a silicon solar cell (New-Spec). Electrochemical measurements were carried out using PG 310 potentiostat from HEKA Electronics (Lambrecht/Pfalz, Germany). Electrolysis experiments were performed using a sealed three-electrode Teflon PEC cell consisting of a platinum counter electrode, Ag/AgCl 3M KCl reference electrode and the working electrode (SiNWs with {Ni_4O_4} clusters). The working electrode was illuminated with a light intensity of 100 mW/cm^2 under air mass 1.5 conditions with short 12 s dark and 12 s light cycle to measure the photocurrents for 5 min. The potential between the working and reference electrodes was adjusted between 0 and −500 mV in 100 mV steps. The 5-h photocurrent run was measured using a light cycle at a bias voltage of −500 mV with respect to the open circuit potentials (OCPs). In order to measure H_2, the sample gas in the headspace (500 μL) above the electrolyte was sampled after 1 h and analysed using a SRI 310C series GC with a thermal conductivity detector and a column held at 70 °C using N_2 as the carrier gas.

Surface Characterisation:

Scanning electron microscopy (SEM) images were obtained using an FEI Quanta 450 environmental scanning electron microscope (Hillsboro, OR, USA). X-ray photoelectron spectroscopy (XPS) measurements were recorded on a Thermo Scientific K-alpha spectrometer (Staffordshire Technology Park, Stafford, UK) at University College London.

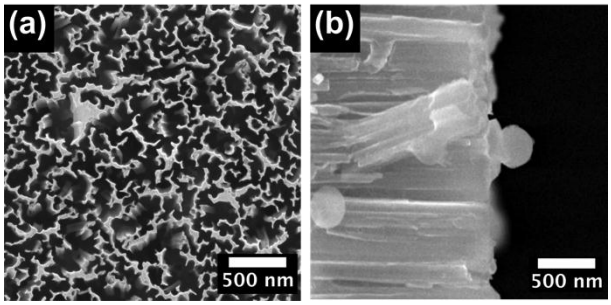

Figure S1. (**a**) Top down SEM for SiNW photocathodes (bare); (**b**) shows a cross section SEM of the SiNWs with {Ni_4O_4} co-catalyst.

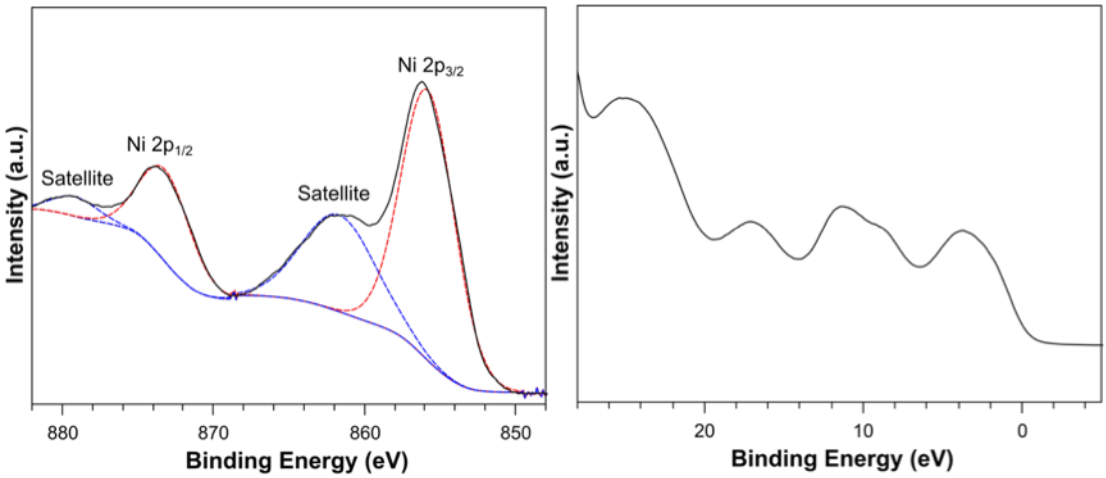

Figure S2. Ni 2p XPS spectra of {Ni_4O_4} clusters (**left**), valence spectra for Ni 2 p (**right**).

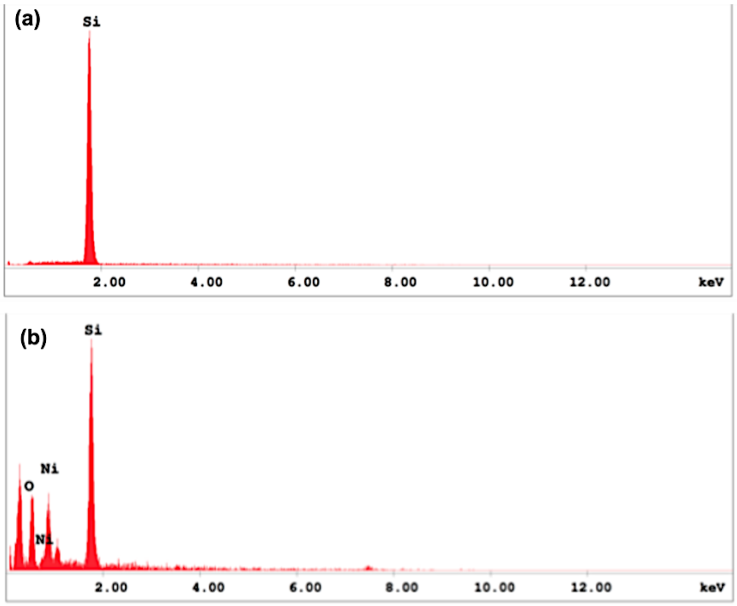

Figure S3. EDS spectra of (**a**) bare SiNWs and (**b**) SiNWs + {Ni_4O_4} clusters.

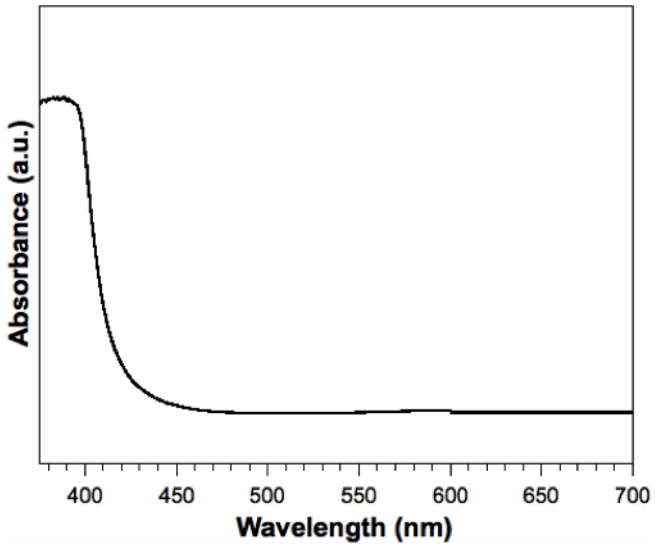

Figure S4. UV-visible spectroscopy of {Ni_4O_4} clusters.