Supporting information

Photoelectrocatalytic CO_2 reduction with plasmon hot-carriers

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Sample preparation:

Au naniparticles (NPs) synthesis:

Sodium citrate tribasic dihydrate 50 mL (6.6 mM) water solution was taken in a 100 mL round bottom flask and stirred at 70^{o}C on an oil bath. Then 0.1 mL (2.5 mM) tannic acid was added to the reaction mixture. Finally, 1mL of (25 mM) $HAuCl_4$ was added instantly. After 5 minutes the reaction mixture colour changed from dark blue to wine. The change in colour confirms the formation of the Au nanoparticles. The synthesized Au nanoparticles were stored in a fridge. The size of the Au nanoparticles was analysed using dynamic light scattering (DLS.

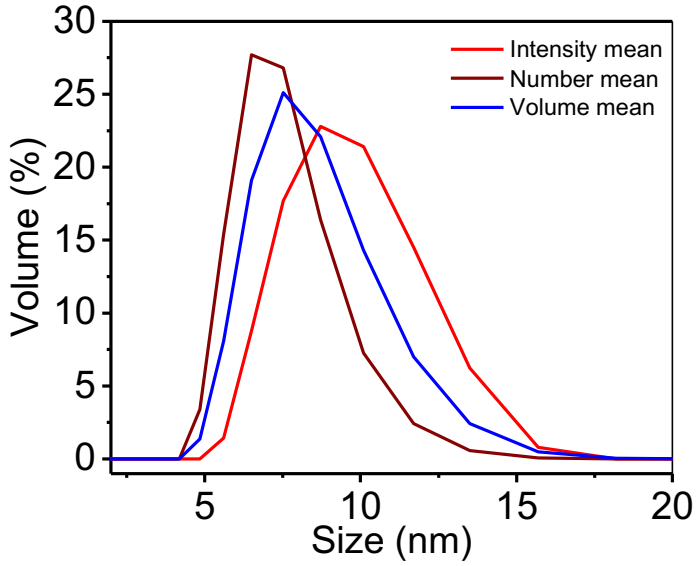

FIGURE S1: Dynamic light scattering (DLS) analysis of Au NPs in water.

Re^{I}(phen-NH_2)$(CO)_3Cl$ (phen-NH_2 = 1, 10-Phenanthrolin-5-amine) catalyst synthesis:

1, 10-Phenanthrolin-5-amine 200 mg (1.02 mmol) and pentacarbonylchlororhenium (I) 368.94 mg (1.02 mmol) were suspended in 40 mL toluene using a 100 mL round bottom flask. The reaction mixture was stirred at 110°C for 6 hours. Then the reaction mixture was cooled down to room temperature. The obtained yellow colour precipitate was filtered using a G4 gooch crucible under vacuum and finally washed 3 times with 50 mL toluene. Yield 379.57 mg (74%). ^{1}H NMR (400 MHz, DMSO-d_6): δ ppm 9.38 (1H, dd, J = 5.2, 1.2 Hz), 9.12 (1H, dd, J = 8.8, 1.2 Hz), 8.94 (1H, dd, J = 4.8, 1.2 Hz), 8.49 (1H, dd, J = 8.4, 1.2 Hz), 8.06 (1H, dd, J = 8.6, 5.2 Hz), 7.79 (1H, dd, J = 8.4, 5.2 Hz), 7.07 (1H, s), 6.89 (2H, s).

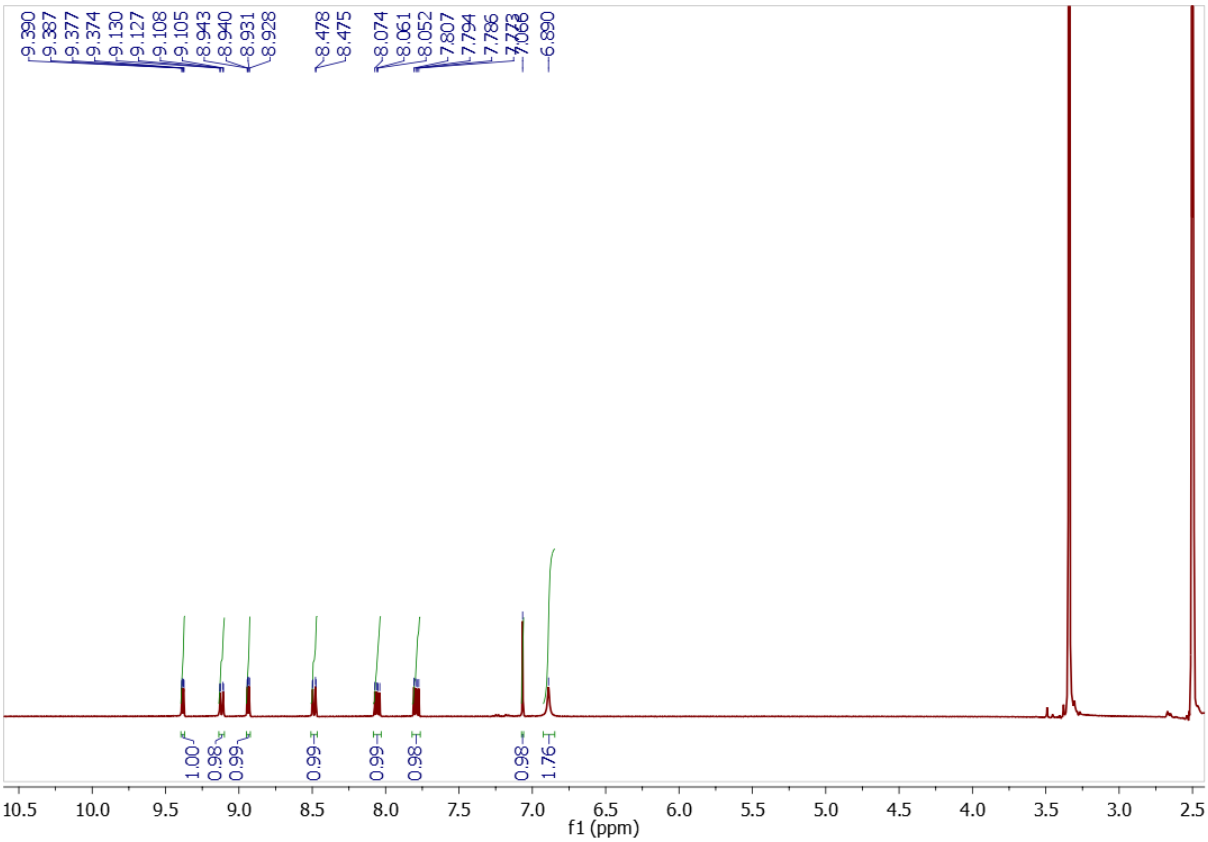

FIGURE S2: ^{1}H Nuclear magnetic resonance (NMR) spectrum of Re^{I}(*phen-NH*$_2$)$(CO)_3Cl$ in DMSO-d_6.

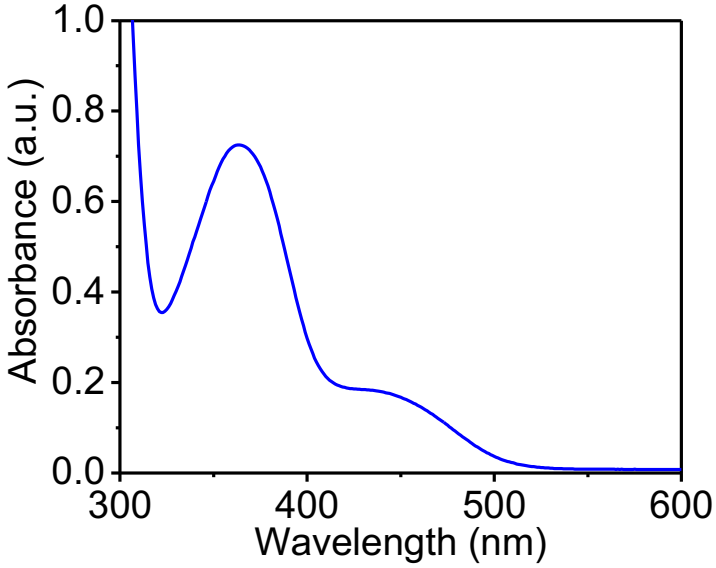

FIGURE S3: Optical spectrum of Re^{I}(*phen-NH*$_2$)$(CO)_3Cl$ in Dimethylformamide.

Preparation of the thin films:

The preparation and process of NiO film:

The NiO paste was purchased from Solaronix and used as received. A small portion of the NiO paste was placed on a screen, placed on top of the cleaned FTO glass and manually printed on conducting side of the FTO glass. Then the NiO-printed FTO glass plates were annealed at 500^{o}C for 1 hour at a rate of 10^{o}C/minute.

Assembly of the Au nanoparticles on NiO film:

The synthesised Au nanoparticles were sprayed manually on NiO films and annealed at 500^{o}C for 1 hour at a rate of 10^{o}C/minute.

Assembly of the catalyst on NiO/Au surface:

The annealed NiO-Au films were dipped into a 2mg/mL solution of the synthesised Re^{I}(*phen-NH_2*)$(CO)_3Cl$ catalyst in Dimethylformamide for 48 hours. Finally, we could get the self-assembled NiO/Au/Re^{I}(*phen-NH_2*)$(CO)_3Cl$ composite system. For experimental purposes, we have also sprayed Au nanoparticles only on FTO glass.

Samples characterization:

The UV-Vis spectra were collected using a cary 5000 UV-VIS-NIR spectrophotometer. The dynamic light scattering (DLS) data was carried out in a Zetasizer nano series nanoS instrument and a total of 3 measurements comprised of 12 scans each time was done. The ^{1}H NMR was measured using a JEOL 400 machine. FT-IR spectrometer FT-IR data were measured using a universal ATR sampling assembly on a VERTEX 70v instrument. The electrochemical data were measured using a EmStat potentiostat instrument. For the electrochemical experiments, a typical cylindrical closed cell was used. The FTO films were placed on the side of the cell so that it could face the light. The 532 nm, 100W continuous wave laser was used during the CO_2 reduction experiment. Pt wire counter electrode and Ag/AgCl (0.1 M $TBAPF_6$/acetonitrile) reference electrode were purchased from redoxme and used as received. Tetrabutyl ammonium hexafluorophosphate purchased from MeRCK was used as a supporting electrolyte without further purification.

XPS and HAXPES measurements:

Photoelectron spectra were recorded using two photon energies, Al Kα (1487 eV) and Ga Kα (9.25 keV). The electron energy analyser used was an Scienta Omicron EW-R4000. The spectra were recorded in a wide region between 0 and 100 eV electron binding energy giving a large

difference in information depth for the two photon energies. The samples were measured as thin films on conductive glass.

ICP-OES measurement:

The Inductively coupled plasma - optical emission spectrometry (ICP-OES) has been used to estimate the actual concentrations of the rhenium in the sample. The film was digested four couple of hours in 4 ml of Nitric acid (Nitric acid 65%, FisherScientific), small probe was diluted 10 times with milliQ water containing 5% HNO_3 and filtered with 0.2 μm syringe filters (Whatman) before measurement. Avio 200 Scott/Cross-Flow Configuration was used for ICP measurements. A calibration curve was formed for the measurements using a Rhenium Calibration Standard (Merk). Concentrations of 0, 0.1, 1 and 10 ppm of the Re were used to create a 4-pointlinear regression. All measured values are within a *relative standard deviation* (RSD) of 2%.

Transient absorption spectroscopy (TAS)

Briefly, a 40-fs pulsed laser with a 3 kHz repetition rate was generated through the Libra Ultrafast Amplifier System designed by Coherent. An optical parametric oscillator (TOPAS-prime, Light Conversion) was used to generate the excitation beam. The signals were detected with a UV-NIR detector, namely a Newport MS260i spectrograph with interchangeable gratings. The fundamental laser (probe, 795 nm) passes through the delay stage (1-2 fs step size) and is focused in a Sapphire optical window in order to generate visible light from 400 to 750 nm. The instrument response function obtained for our system is ca. 95 fs.

Transient infrared absorption spectroscopy (TIRAS)

Briefly, a 40-fs pulsed laser with a 3 kHz repetition rate was generated through the Libra Ultrafast Amplifier System designed by Coherent. Two optical parametric oscillators (TOPAS-prime, Light Conversion) were used to generate either the excitation beam and/or the probe light in the Mid-IR (3000-10000 nm). The signals were detected with a Horiba iHR 320 spectrometer. The pump laser power was constantly monitored with less than a 2% standard deviation. The timing resolution, i.e., the instrument response function is ca. 100 fs.

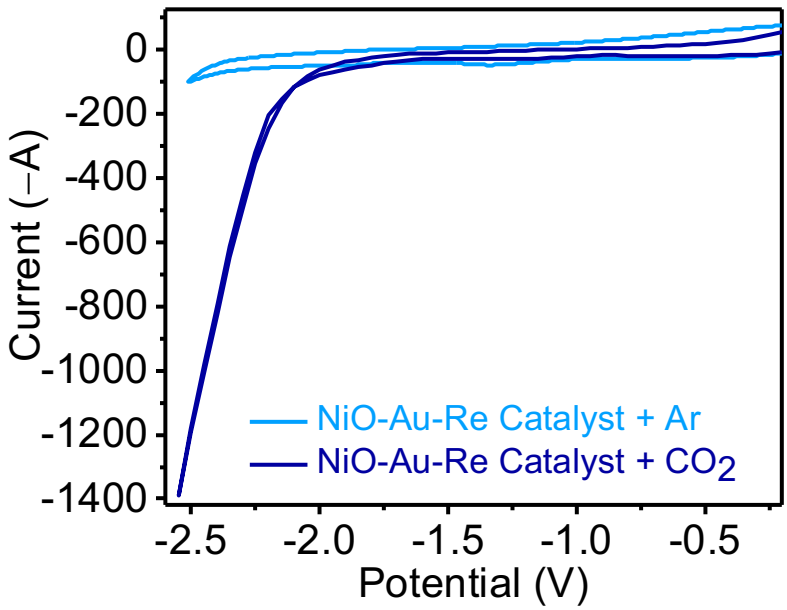

FIGURE S4: Cyclic voltammograms of the NiO/Au/Re^{I}(*phen-NH$_2$*)(CO)$_3$Cl in argon and CO_2 purging conditions.

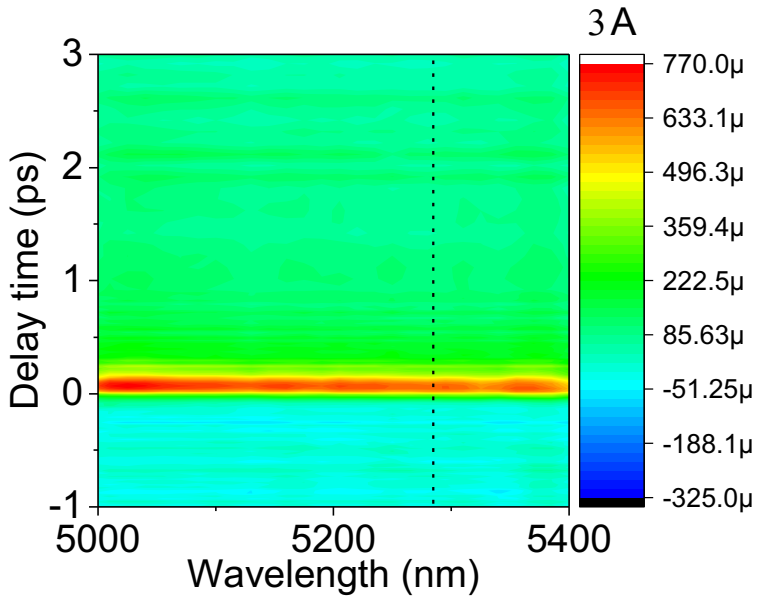

FIGURE S5: TIRAS contour plot of NiO/Au/Re^{I}(*phen-NH$_2$*)(CO)$_3$Cl in the carbonyl region.