Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Understanding the Catalyst-Photocathode Interfaces to Enable High Performance Earth Abundant HER Catalysts

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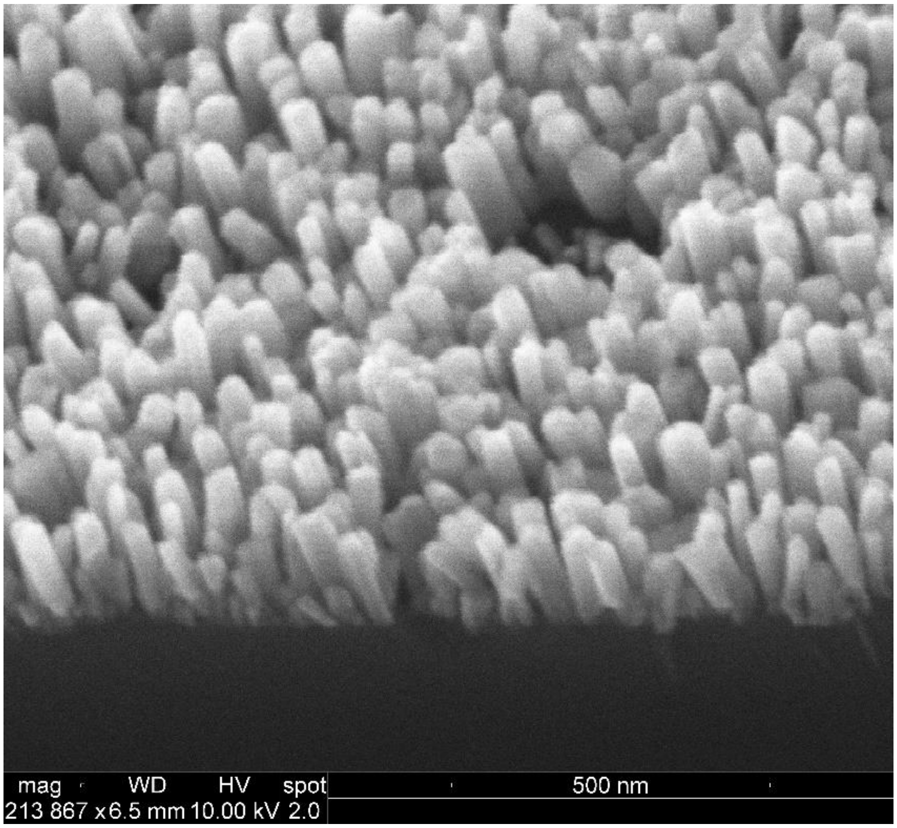
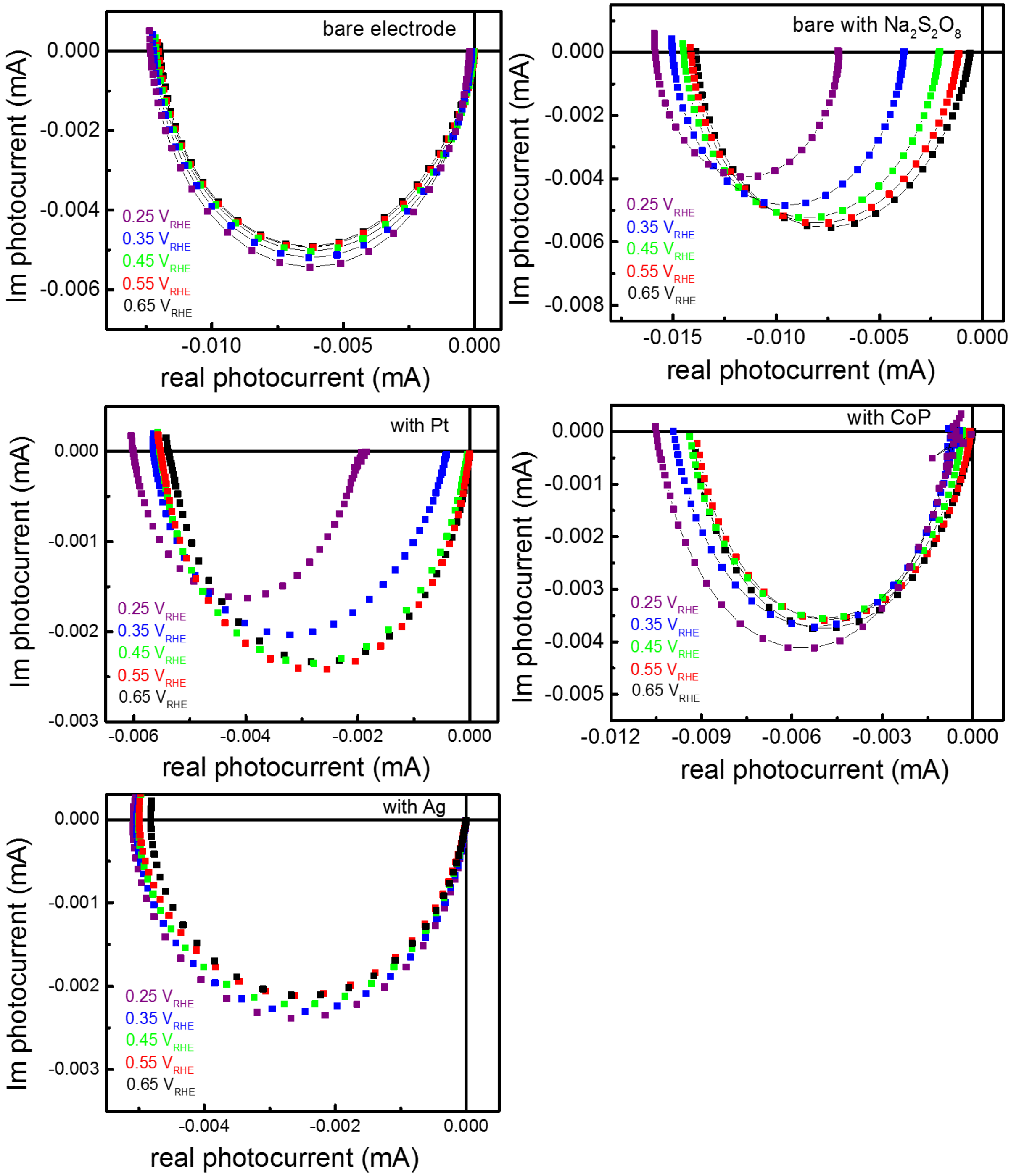
Figure S1. SEM image of the photocathode used for this study.



The dark park on the bottom of the image shows the Si substrate. The white pillars show the n-GaN nanowires that were grown on top of the Si.

Figure S2. Representative raw IMPS data of each of the systems tested for this study.



As expected, the bare electrode is dominated by recombination as the low frequency rate constant goes almost to 0 photocurrent at all applied potentials. When the electron scavenger is added to the bare electrode the radial frequency is not changed. However, the low frequency intercept is greatly increased at higher applied potentials as compared with the bare electrode. This indicates that the k_{tran} is being increased while the k_{rec} remains unchanged. The addition of Pt to the surface of the photocathodes greatly reduces the recombination rate constant (see figure S3). Additionally, as the charge transfer increases so does the low frequency intercept. With CoP on the surface of the GaN NWs the recombination does not change at low allied potentials, but at high applied potentials the recombination rate constant drastically decreases and the charge transfer begins to increase, as seen by the increase in the low frequency intercept. The addition of Ag to the photocathodes looks much like the bare electrode. However, the Bode plot (figure S3) shows that the resonant frequency is much lower. Since the low frequency intercept is essentially zero for the bare and electrode with Ag, the resonant frequency can be associated with the recombination rate constant.

Figure S3. Representative Bode plots as measured by IMPS at 0.65 V vs RHE.

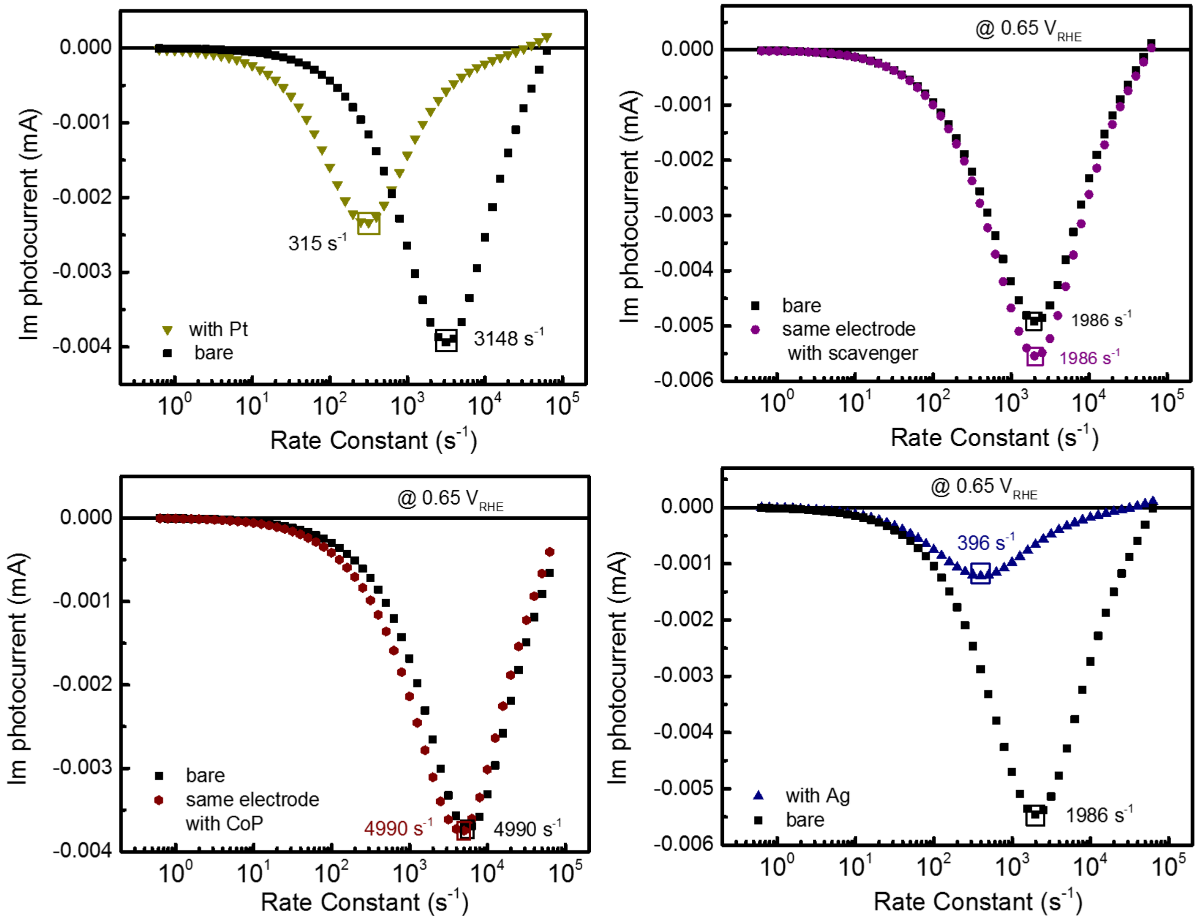
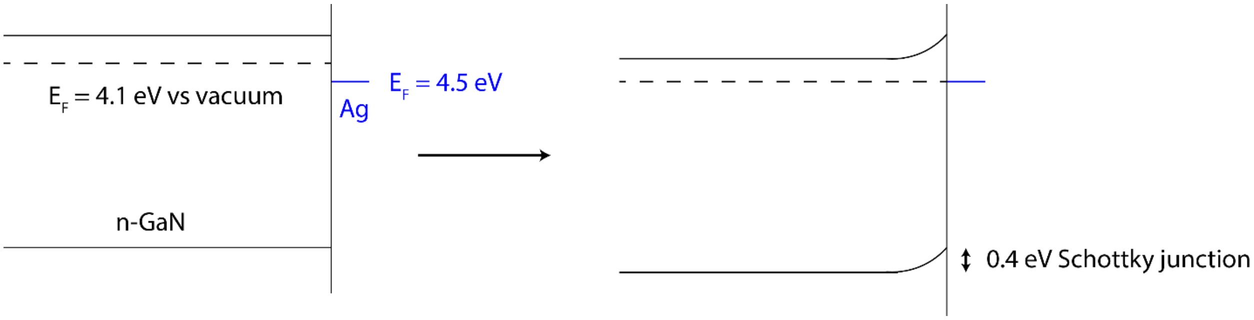
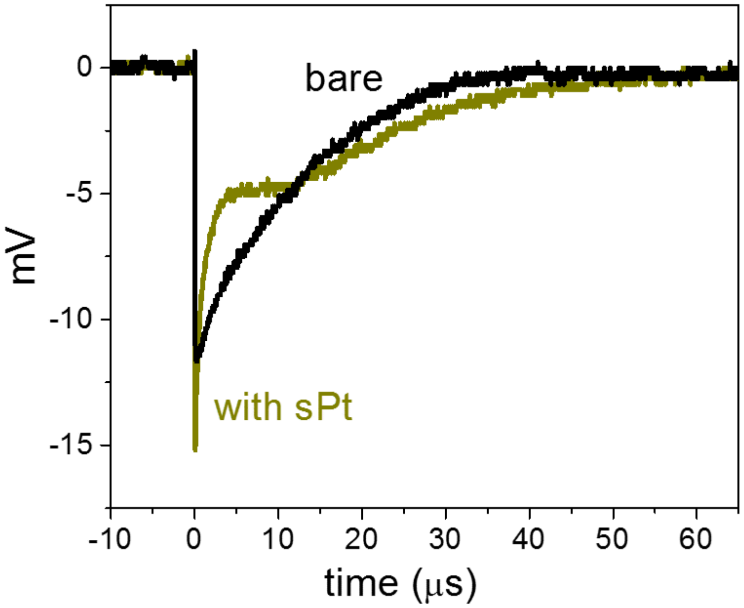


Figure S4. Schematic band diagram of the Schottky junction that forms with the addition of Ag to the surface of n-GaN nanowires.



The Schottky barrier will act as an electron trap for electron that transfer to Ag. This explains the large decrease in the recombination rate constant with the addition of Ag. Pt will also form a Schottky junction with n-GaN and since its work function is well above 5 eV the barrier will be much larger. This is also consistent with the recombination rate constants that we measured in this study, where recombination was typically lower with Pt rather than Ag.

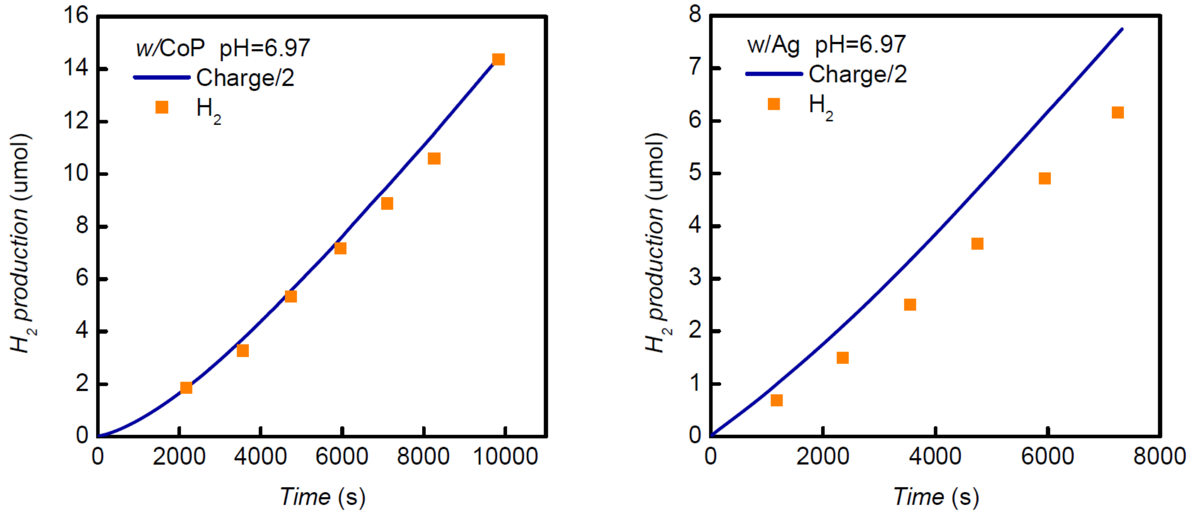
Figure S5. A time resolved microwave conductivity plot of the photocathode with and without Pt. Fitting each sample shows that the addition of Pt to the photocathodes reduces the recombination.



A Quantel Q-Smart 450 Nd:YAG was used at the pump source. A third harmonic generator was used to produce 355 nm light. A fluence of ~50 mJ/cm^2 was used with a time resolution of 6 ns. The probe was a HP 8350B with a HP83570A RF Plug-in was used as the microwave source. The microwave frequency used for these measurements was 20 GHz. A Advanced Control Components ACSP-2644NZC15 microwave detector was used followed by a Stanford Research Systems SR 445A amplifier. A Tektronix TDS 2022B oscilloscope was used to record the change in the voltage with respect to time.

Using a first order decay fit, it was found that the bare photocathode had a recombination time constant of 10 µs. When Pt is added to the photocathode's surface, the time constant is extended to 20 µs. This matches the IMPS impedance analysis of this system, as the addition of Pt extends the charge lifetime. In addition, the presence of Pt also give rise to a new time constant with a time constant of about 1 µs. This could arise from two possible scenarios: Pt is further reducing a very fast charge recombination process that for the bare sample is out of the resolution for our pump probe set up, or, alternatively, the addition of Pt is introducing a new charge recombination pathway. For this study, we did not further investigate these possible situations, but we note that this could be an interesting future study.

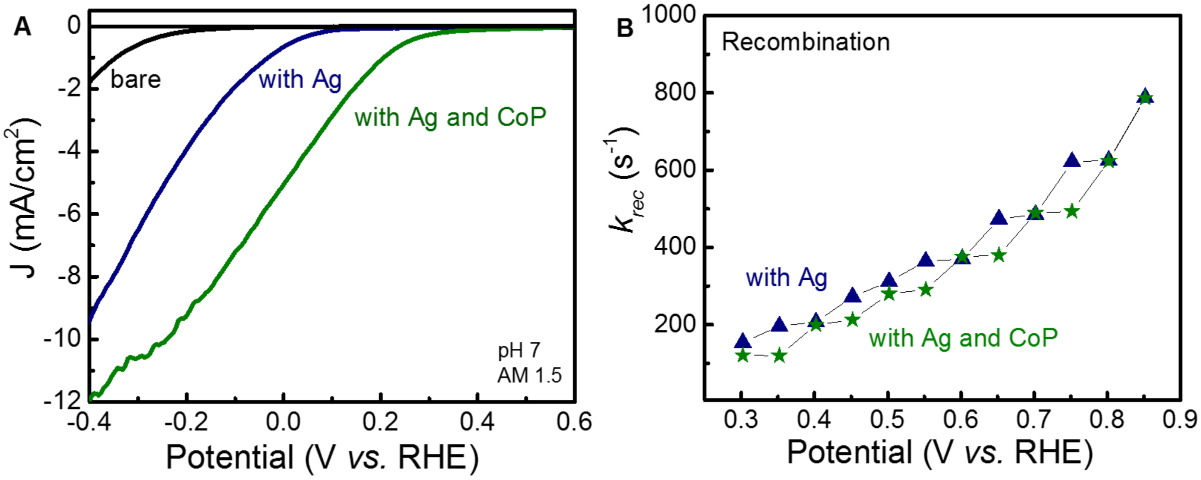
Figure S6. Faradaic efficiency plots of the photocathodes modified with CoP and Ag.



H_2 detection was carried out in a sealed three-neck flask under 0 V vs. RHE applied potential with different working electrodes. Three electrode configuration was employed similar to the PEC tests. UHP-grade He was used to purge the cell for at least 60 min in order to remove residual gases in the electrolyte before the measurement. A gas sample of 100 μL, from the head space of the flask, was injected manually to GC-MS (Shimadzu QP2010 Ultra, with Carboxen 1010 PLOT column at 35°C) every 20 min. UHP-grade H_2 was used to calibrate the instrument.

The electrode with Ag did not show 100% Faradaic efficiency. However, since it is known that Ag will capacitively accept charges, the differences between the detected product and the charge passed could come from the charging of the Ag nanoparticles. Regardless of the product, Ag forms a Schottky junction with n-GaN and will reduce recombination and shift the onset potential. This confirms that the addition of Pt to the surface of the photocathodes serves the dual purpose of reducing recombination as well as catalyzing the HER.

Figure S7. A) JV curve of and electrode with Ag and the same electrode with CoP deposited on top. B) The recombination rate constant of the electrode with Ag before and after the CoP deposition.



We indeed tested the addition of CoP to an electrode with Ag. This could possibly represent a system where the charge recombination is being controlled by the Ag on the surface of the photocathode and the HER charge transfer was controlled by the CoP, thus creating a Pt like earth abundant system. However, we found that while the addition of CoP does indeed improve the onset potential of the system, and that the k_{rec} is controlled by the Ag, the onset potential of the electrode with Ag and CoP does not improve past the onset potential of the electrode with just the CoP. This is possibly due to the capacitive nature of Ag, meaning that while the Ag is forming a Schottky junction and reducing the recombination it will not form an Ohmic contact with CoP and therefore the charges will stay localized on the Ag. The CoP in this system, deposits on top of the Ag NPs as well as on the bare GaN. The charge transfer pathway for HER will then predominantly go through CoP.

Figure S8. The addition of $Na_2S_2O_8$ to the electrode with Pt further increases the photocurrent and the onset potential of the electrode, while the measured k_{rec} remained unchanged. This further demonstrates that the measured k_{rec} can be separated from the surface kinetics.