Supporting Information

Critical Coupling of Visible Light Extends Hot-Electron Lifetimes for H₂O₂ Synthesis

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**S1: Additional Experimental Methods**

*Atomic Layer Deposition*

We carried out atomic Layer deposition (ALD) in a viscous flow reactor (GEMSTAR, Arradiance). Ultrahigh-purity N$_2$ was used as the carrier gas at a flow rate of 100 mL min$^{-1}$. We loaded the substrate into the ALD chamber, and the ALD TiO$_2$ over-coats were grown by sequentially exposing the film to titanium isopropoxide (TTIP, Strem, 98 %) and H$_2$O (millipore water) at 225 °C. TTIP stored in a stainless-steel bubbler was heated to 80 °C to achieve a sufficient vapor pressure. Each ALD cycle includes a 700 ms TTIP exposure, a 23 s N$_2$ purge, a 22 ms water exposure, and a 28 s N$_2$ purge. We repeated the cycle 360 times in order to attain a ~10 nm TiO$_2$ layer.

*Gold Photodeposition:*

The gold photodeposition process used was adopted from Waclawik *et al*. We diluted a 10 mM stock solution of HAuCl$_4$ in ethanol to 0.5 mM (20 ml) and then exposed to a continuous UV-A light (350 nm – 390 nm) of 40 mW cm$^{-2}$ intensity for 20 min to fully “pre-irradiate” the solution and form HAuCl$_2$. Completion of the pre-irradiation was confirmed by observing the solution color change from light-yellow to clear, with confirmation via UV-Vis spectroscopy of the absorbance decrease at 320 nm, which corresponds to the ligand-to-metal charge transfer absorption band for AuCl$_4$. This pre-irradiated solution was used immediately, though shown to remain stable for at least 48 hours. Pre-irradiation for longer than 60 min was shown to form fully-reduce Au nanoclusters which agglomerated and dropped out of solution.
We immersed samples with ZnO films in 7.5 ml of the pre-irradiated gold solution in a 50 ml beaker. We shook the beaker at 80 rpm under a pulsed UV-A illumination of 30 W m\(^{-2}\), with a pulse pattern of 5 sec on + 5 sec off repeated for a full 60 seconds. Samples were then removed from the solution, rinsed with ethanol, and dried with N\(_2\). The sample surface exhibited a consistent purple color, with the absorbance profile confirmed via UV-Vis spectroscopy in an integrating sphere.

**Material Characterization – SEM, XRD, and ICP-OES:**

We analyzed the morphology of samples with a FEI Quanta 3D scanning electron microscope (SEM), employing both secondary electron (SE) and backscattered electron (BSE) detectors. We used a SE detector to image the morphology of the ZnO film and size of Au nanoparticles, while the BSE detector enhanced the atomic number contrast, permitting better differentiation between the Au nanostructures and underlying ZnO film.

The crystal structure of our ZnO films was identified through out-of-plane XRD using a PANalytical X-ray diffractometer operating at 45 kV and 40 mA. The 0-20 radial scan was performed over the range 30-45° with a step size of 0.01° and dwell time of 120 s, using Cu K\(_\alpha\) (\(\lambda=1.54\) Å) as the radiation source.

We quantified the Au and ZnO mass composition of our samples with a PerkinElmer Optima 8000 Optical Emission Spectrometer (OES). Samples for OES measurement were digested in 10 ml Aqua Regia and the resulting solution was diluted with 40 ml of de-ionized water. Metal standards (Au, Zn) were purchased from BDH (VWR Analytical) and diluted to the measurable
range with a similar HCl/HNO₃ acid matrix as the experimental solutions. The linear fit of each standard was $> 0.9999$ across a concentration range spanning 3 orders of magnitude.

**Finite Element Method Simulations:**

We used the Maxwell equation solver JCMsuite v3.18 (JCMwave GmbH) to calculate the absorption in the various layers of the MIM structure as a function of wavelength and ZnO thickness. JCMsuite uses hp-refined finite element method to solve for the full electromagnetic field. We used a polynomial degree of four for all electromagnetic simulations. Typical meshes for the geometries are shown in Fig. 2a. We modeled the Au nanoparticles as isolated structures with a perfectly matched layer (PML) on all boundaries of the mesh; PML thickness was tuned by JCMsuite’s internal algorithm. We excited all geometries with normal incidence plane waves and TM and TE polarizations. Due to the symmetry of the geometry the polarization did not affect the results.

**Ultrafast Pump-Probe Spectroscopy, cont.:**

The time-resolved spectroscopic data was first processed using Surface Xplorer software to correct for any artifacts introduced by temporal dispersion of the probe (chirp). Time zero was identified for four different wavelengths, then a third order polynomial was fit to the data points to correct for time zero over the full spectrum. This procedure was performed for both transmission and reflection data sets.
A FLIR Blackfly photodiode camera was used to capture the pump and probe profile and a Gaussian function was used to extract the FWHM of the pump and probe beams to measure fluence using an effective area of the overlap of the pump and the probe:

\[ A_{\text{eff}} = \frac{\pi}{\ln(2)} (\text{FWHM}^2_{\text{pump}} + \text{FWHM}^2_{\text{probe}}) \]

The FWHM at the sample position were 157 µm for 600 nm pump, 164 µm for 540 nm pump, 150 µm for 535 nm pump, 192 µm for 500 nm pump, 179 µm for 450 nm pump, 225 µm for 330 nm pump, and ~90 µm for the probe.

**Ultraviolet Photoelectron Spectroscopy (UPS):**

We performed ultraviolet photoelectron spectroscopy (UPS) measurements at the 5-meter toroidal grating monochromator (5m-TGM) beamline at the Center for Advanced Microstructures and Devices (CAMD) at Louisiana State University, described in detail elsewhere.\(^1\) The beamline is equipped with an ultrahigh vacuum (UHV) chamber endstation, which carries an Omicron EA125 hemispherical electron energy analyzer with a five channel detector. The endstation was kept under UHV with a pressure of \(10^{-10}\) mbar. The samples were held on tantalum holder by placing two tantalum stripes over the films. All samples were gently sputtered (1 keV Ne\(^+\) for 2 minutes at \(1\times10^{-5}\) Torr) to remove the contaminants from the surface. All spectra were collected in normal emission geometry and normalized to a point on the background formed by inelastic secondary electrons. UPS spectra were collected with a constant pass energy of 10 eV and a photon energy of 65 eV. The binding energies in UPS spectra are referenced with respect to the Fermi level of a gold foil in electrical contact with the sample holder.
S2: Optical Data

Figure S1: Measured optical properties (real and imaginary permittivity) of ZnO and TiO$_2$ through spectroscopic ellipsometry.

Figure S2: Ellipsometer fit for TiO$_2$ ALD – 360 cycles. Fit parameters: thickness = 10.21 nm,
Mean Standard Error (MSE) = 1.569
Figure S3: Ellipsometer fit for ZnO Sol-Gel (50nm). Fit parameters: thickness = 52.51 nm, MSE = 8.382

Figure S4: Optical properties of Al Film (~ 300 nm) evaporated on EXG
A Tauc plot is used to determine the optical band gap of our semiconductor films. The photon energy ($h\nu$) is plotted versus the quantity $(\alpha h\nu)^{1/r}$, where $\alpha$ is the absorption coefficient and $r$ represents the optical transition. For TiO$_2$, an indirect bandgap semiconductor, $r = 2$ whereas ZnO has a direct bandgap and thus $r = ½$.

Figure S5: Tauc plots to estimate the band gaps of ZnO and TiO$_2$ films
Figure S6: Simulations of various optical coupling regimes (simulated in water), including a) near-field coupling, b) critical coupling, and c) Fabry-Perot cavity. Panel d) is reproduced from Figure 2e in the paper for reference.

Figure S7: Experimental absorption data (in air) with varying ZnO thicknesses. Controls include a) ZnO only, b) Au-(ZT), and c) Au-(ZT)-Al, where the thickness indicated is only for the ZnO layer.
S3: XRD and Scherrer Equations to estimate ZnO grain size

The Scherrer equation can be used to estimate the grain size of crystalline materials by:

\[ \tau = \frac{K\lambda}{B \cos \theta} \]  

(Equation S1)

Where \( \tau \) is mean size of ordered (crystalline) domains, \( K \) is dimensionless shape factor (assumed to be 0.9 here), \( \lambda \) is the X-ray wavelength (Cu k\(_{\alpha1} \) = 1.5416 Å), \( B \) is the full-width half max (FWHM) in radians, and \( \theta \) is the Bragg angle. With XRD, we examined the (100), (002), and (101) orientation peaks of our wurtzite ZnO and performed a Gaussian fit to calculate \( B \), and by extension \( \tau \). The same test was performed on two samples, the data for which is represented in Figure S8. The ZnO grain size, averaged across both samples and all orientations, is estimated to be 12.1 ± 2.9 nm. Note the sharp peak at \( 2\theta \approx 38.5^\circ \) represents the (111) orientation of the Al substrate upon which the ZnO was spun.

Figure S8: XRD of ZnO on Al with Gaussian peak fits for the ZnO (100), (002), and (101) orientations. Samples A (a) and B (b) are replicates with the same sample preparation.
In addition to the description of Au photodeposition provided in section S1, we adjusted parameters of 1) the initial HAuCl₄ concentration, 2) pulse parameters (on / off time) and 3) overall pulse time. For our ZnO-based samples, a HAuCl₄ concentration < 1 mM and minimum overall pulse time were desired to mitigate ZnO dissolution in the acidic medium. Furthermore, the pulse parameters chosen provided more consistent Au nanoparticle sizes than a non-pulsed (continuous) UV illumination, which are shown in Figure S10.
Figure S10: SEM images for Au photodeposition on (ZT)-Al with continuous UV exposure times of a) 1 min, b) 3 min, and c) 5 min.

As observed in the Figure S11, utilizing a back-scatter detector with our SEM imaging provided better clarity between the Au nanoparticles and ZnO film. Using ImageJ software (freely available online), we adjusted the image contrast and binarized the image to select the Au domains (Figure S10). Further filtering of particles based on overall size (> 2 nm diameter and < 80 nm) and circularity (> 0.6) were used to eliminate artificial Au clusters from the particle size analysis. Results for Au nanoparticle size were binned in 5 nm size increments for three images of varying magnification. For each image, the number of particles analyzed was > 500.
Figure S11: SEM micrographs of Au-(ZT)-Al samples using a) SE detector and b) back-scatter detector (BS-SEM).

Figure S12: BS-SEM images of Au-(ZT)-Al a) before and b) after binarization in ImageJ.

Particle analysis from binary images were used to estimate the Au nanoparticle size distribution.
Figure S13: BS-SEM images of Au-(ZT)-Al at a) 150,000x, b) 80,000x, and c) 50,000x magnification. The respective histograms of particle size distribution, along with their average and standard deviation, are provided below each image (d,e,f).
S5: ICP-OES measurements of Au loading

To determine the mass loading of Au, we started by estimating and measuring the total mass of ZnO in our samples. The ZnO mass estimate was based on the measured 50 nm ZnO thickness, which over a 2.54 cm x 2.54 cm samples corresponds to 3.125 x 10^{-5} cm^3 volume of ZnO. Given the average density for ZnO of 5.61 g cm^{-3}, we estimated ~175.3 μg of ZnO to be present on any of our samples. This would correspond to a Zn^{2+} ion total of ~ 140.25 μg after complete etching of the ZnO in a solution of aqua regia. Measurements of Zn ion concentration aqua regia etched samples provided an average mass of 136.7 μg, which is very close to the estimated mass loading of ZnO.

For Au mass, we performed photodeposition of Au for 60 sec on 4 sets of 4 samples with different loadings of ZnO: 25 nm, 50 nm, 75 nm, and 100 nm. This was to determine if the mass of ZnO, and therefore the extent of UV absorption during the photodeposition process, had any effect on the Au mass loading. Samples were then etched in Aqua regia, diluted, and immediately analyzed via ICP-OES. The data suggests that, apart from a slight decrease in Au loading with 25 nm ZnO, the Au mass loading during ZnO is largely independent of the ZnO thickness. For 50 nm ZnO, the average Au mass in μg was measured to be 37.7 ± 2.6 μg. Therefore, the mass loading of Au on 50 nm ZnO was calculated to be 18% (w/w). Note this loading would decrease if the TiO_2 or Al layers are considered.
Figure S14: Mass loading of Au on (ZT)-Al samples of varying ZnO thicknesses as determined via ICP-OES after etching in aqua regia.
The two-temperature model, adapted from Sun et al.\textsuperscript{2} is based on Equation S2:

\[
\frac{\Delta R}{R}(\hbar \omega, t) = H(t) \left\{ \right.
\left. \frac{\Delta R}{R} \big|_{NT}(\hbar \omega) \exp \left( -\frac{t}{\tau'_{th}} \right) \right.
\left. + \frac{\Delta R}{R} \big|_{Th}(\hbar \omega) \left[ 1 - \exp \left( -\frac{t}{\tau_{th}} \right) \right] \exp \left( -\frac{t}{\tau_p} \right) \right.
\left. + \frac{\Delta R}{R} \big|_{L}(\hbar \omega) \right\} \quad \text{(Equation S2)}
\]

Where \( H(t) \) is the Heaviside function, \( \tau'_{th} \) is the decay time of the nonthermal population, \( \tau_{th} \) is the thermalization time, \( \tau_p \) is the time constant for electron-phonon interaction, and the transient reflection (or absorption or transmission) signal is denoted by \( \frac{\Delta R}{R} \) and separated into non-thermal (NT), thermal (Th) and lattice relaxation (L) components. A best fit was determined by minimizing the \( \chi^2 \) value of parameters assuming a non-thermal decay time < 200 fs and a starting guess of e-ph coupling time of 1 ps.
Figure S15: Plots of dT/T for selected samples of a) Au-(ZT)-Al and b) Au-(ZT) pumped at 530 nm and probed at 535 nm with varying pump intensities. The e-ph coupling is fit by the two-temperature model.

Figure S16: Transient absorption spectra for Au-(ZT)-Al samples pumped at a) 700 nm, b) 600 nm, c) 530 nm, d) 500 nm, and e) 450 nm. Corresponding kinetic rise and decay of the Au bleaching at 535 nm and ZnO population at 366 nm are provided in f-j. Photon flux was normalized to $2.6 \times 10^{15}$ photons per pump pulse to allow direct comparison of kinetics.
Quantitative data for the Au e-ph coupling times (fit by TTM) and ZnO rise time is provided in Table S1.

Table S1: Au e-ph coupling time & fit parameters, along with ZnO rise times for Au-(ZT)-Al samples under varying pump wavelengths (and Au-(ZT) at 530 nm for comparison). Visible pumps were conducted with a photon flux of $2.6 \times 10^{15}$ photon cm$^{-2}$, and a flux of $4.8 \times 10^{14}$ cm$^{-2}$ was used for the UV pump.

| Sample | $dT/T |_{NT}$ | $\tau_{th}$ (ps) | $dT/T |_{Th}$ | $\tau_{e-ph}$ (ps) | $dT/T |_{L}$ | $X^2$ | Rise Time (ps) |
|--------|-----------|-----------------|---------------|----------------|---------------|--------|----------------|
| 700 nm | -0.0068   | 0.200           | 0.0120        | 1.97           | 0.0010        | 5.82E-06| 0.99           |
| 600 nm | 0.0023    | 0.197           | 0.0370        | 3.49           | 0.0053        | 1.19E-04| 0.67           |
| 530 nm | -0.0360   | 0.152           | 0.0472        | 6.02           | 0.0130        | 4.33E-04| 1.88           |
| 500 nm | -0.2133   | 0.123           | 0.0484        | 5.42           | 0.0127        | 2.31E-04| 1.92           |
| 450 nm | -0.0549   | 0.198           | 0.0395        | 3.07           | 0.0042        | 6.51E-05| 0.35           |
| 530 nm w/o Al | 0.0043        | 0.120           | 0.0117        | 4.07           | 0.0008        | 8.14E-06| 0.98           |
| 330 nm | --        | --              | --            | --             | --            | --     | 0.49           |
Figure S17: Various pump-probe controls, including (ZT)-Al samples (no Au) pumped at a) 450 nm and b) 500 nm, along with c) an Au control sample consisting of Au nanoislands on quartz (formed by evaporating 3 nm Au and dewetting at 400 °C for 1 min) photoexcited at 530 nm. The lack of transient absorption in a and b indicates that ZnO is not activated by visible light, while the Au control confirms that the 366 nm bleach signal ascribed to ZnO does not originate from Au. Furthermore, kinetic traces at 366 nm and the maximum UV bleach is provided for d) 600 nm and e) 530 nm pumps of Au-(ZT)-Al samples, and displays negligible change in data, reaffirming our use of 366 nm to probe the ZnO excitation. A 330 nm pump of (ZT)-Al (f) shows no signal in the visible regime.
Figure S18: Overview of method used to calculate electron injection efficiency in Figure 5b. The maximal Au bleach signal at 535 nm is provided for a) Au-(ZT) and b) Au-(ZT)-Al samples under vary pump intensities. These are plotted with a linear fit in c) and d) in comparison to maximal bleach data collected at 366 nm from ZnO samples pumped at 330 nm for c) EXG and d) Al substrates. The ZnO bleaching under UV pump is assumed to have a quantum efficiency of 1, and the ratio of slopes for maximal signal to photon flux for Au and non-Au samples is used to quantify the electron injection efficiency, similar to Pehrsson et al.³
S7: Photocatalytic Control Tests

Figure S19: Accumulation of H₂O₂ in photoreactor with non-Au catalysts under simulated visible sunlight

Figure S20: Accumulation of H₂O₂ in photoreactor under dark conditions
Figure S21: Accumulation of H₂O₂ in batch system (20 ml volume in 50 ml beaker, shaken at 115 rpm) with low or high dissolved O₂ (D.O.) content. Low D.O. concentration here is ~5.8% of saturation concentration (with N₂ sparging) while high D.O. concentration is 100% saturation with air sparging. Results indicate that the decrease in O₂ leads to a dramatic decrease in H₂O₂ formation, suggesting that the reactions to form H₂O₂ derive from oxygen reduction reaction.
Figure S22: Photograph of Amplex red fluorometric probe during a measurement of H$_2$O$_2$ accumulation.

Figure S23: Residence time distribution, E(t), for our photoreactor as simulated in COMSOL (dotted line) and measured though dye-tracked flow tests (solid line). Flow rate of this measurement is 1 ml min$^{-1}$. 

Figure S24: Steady-state concentration profile of a non-degrading product in our photoreactor. Dimensionality of the photoreactor is also provided. The thickness of the 5 x 5 cm² reaction chamber is 0.5 mm, providing an illuminated reaction volume of 1.25 cm³.

Figure S25: The visible-light irradiance, provided by a filtered solar-simulator, illuminates the reactor with light > 450 nm, nearly matching the AM1.5G solar spectrum.
Figure S26: UPS data for a) TiO$_2$ ALD films and b) ZnO films after light sputtering to remove minor carbon contamination. The valence band maximum (VBM) is determined from the intercept of the extrapolated background signal and the tangent of the inflection point according to the procedure from Kumarasinghe et al.$^4$ for c) TiO$_2$ and d) ZnO, respectively. The VBM is measured to be $\sim 2.9$ eV below the Fermi level for TiO$_2$ and $\sim 3.08$ eV away for ZnO.
Figure S27: UPS data for (a) Au-(ZT)-Al post-sputtering, which is (b) plotted alongside UPS data without Au to determine the initial binding energy and core binding levels. These are used with Equation S3 to determine the effective Schottky barrier height.\(^{5-6}\)

\[
q\Phi_B = E_G - E_V^i + (E_{core}^i - E_{core}^{Au}) = E_G - (E_{core}^{Au} - E_{VC}) \tag{Equation S3}
\]

Where \(E_G\) is the bandgap of ZnO, \(E_V^i\) is the initial binding energy (i.e. VBM), \(E_{core}^i\) is the initial binding energy to the Zn core level (without Au), \(E_{core}^{Au}\) is the binding energy of the core level with Au over layer, and \(E_{VC}\) is the difference of initial binding energy to core level binding.

From the measured values of the parameters through UV-Vis absorbance and UPS, we determine that our effective Schottky barrier height is \(\sim 0.3\) eV.
Supplemental References:

(1) Kizilkaya, O.; Jiles, R. W.; Patterson, M. C.; Thibodeaux, C. A.; Poliakoff, E. D.; Sprunger, P. T.; Kurtz, R. L.; Morikawa, E. High-throughput Toroidal Grating Beamline for Photoelectron Spectroscopy at CAMD. *Journal of Physics: Conference Series* 2014, 493, 012024, DOI: 10.1088/1742-6596/493/1/012024.

(2) Sun, C. K.; Vallée, F.; Acioli, L. H.; Ippen, E. P.; Fujimoto, J. G. Femtosecond-tunable measurement of electron thermalization in gold. *Phys. Rev. B* 1994, 50 (20), 15337-15348, DOI: 10.1103/PhysRevB.50.15337.

(3) Ratchford, D. C.; Dunkelberger, A. D.; Vurgaftman, I.; Owrutsky, J. C.; Pehrsson, P. E. Quantification of Efficient Plasmonic Hot-Electron Injection in Gold Nanoparticle–TiO2 Films. *Nano Lett.* 2017, 17 (10), 6047-6055, DOI: 10.1021/acs.nanolett.7b02366.

(4) Kumarasinghe, A. R.; Flavell, W. R.; Thomas, A. G.; Mallick, A. K.; Tsoutsou, D.; Chatwin, C.; Rayner, S.; Kirkham, P.; Warren, S.; Patel, S.; Christian, P.; O’Brien, P.; Grätzel, M.; Hengerer, R. Electronic properties of the interface between p-CuI and anatase-phase n-TiO2 single crystal and nanoparticulate surfaces: A photoemission study. *The Journal of Chemical Physics* 2007, 127 (11), 114703, DOI: 10.1063/1.2772249.

(5) Das, S. N.; Choi, J.-H.; Kar, J. P.; Moon, K.-J.; Lee, T. I.; Myoung, J.-M. Junction properties of Au/ZnO single nanowire Schottky diode. *Appl. Phys. Lett.* 2010, 96 (9), 092111, DOI: 10.1063/1.3339883.

(6) Hwang, J. D.; Lin, Y. L.; Kung, C. Y. Enhancement of the Schottky barrier height of Au/ZnO nanocrystal by zinc vacancies using a hydrothermal seed layer. *Nanotechnology* 2013, 24 (11), 115709, DOI: 10.1088/0957-4484/24/11/115709.