SUPPORTING INFORMATION

Photooxidative Polymerization of Pyrrole from Photosystem I Proteins

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Attempting Ppy Growth with Chlorophyll a

A 160 µM solution of chlorophyll a and 0.5 M pyrrole was exposed to solar simulated light for 6 h. Here, the concentration of Chl a was selected to approximate that affixed to PSI in solution, assuming 40 chlorophylls per protein on average. After dialysis, an infrared spectrum of the resulting materials (Fig. S1) shows the absence of peaks that are consistent with the growth of Ppy. In contrast, a 4 µM solution of PSI and Py similarly irradiated for 6 h shows the expected peaks for Ppy growth that are consistent with

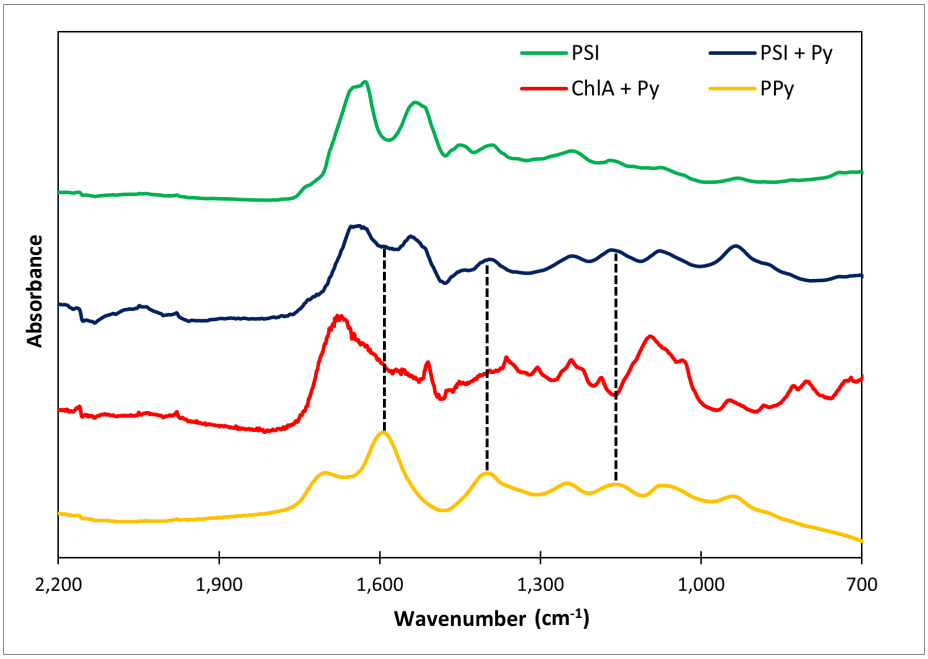

Figure S1 | *Infrared spectra of films prepared from PSI (top), electropolymerized Ppy (bottom), as well as separate spectra for PSI and chlorophyll a that were exposed to Py and $NaClO_4$ under irradiation with a solar simulator for 6 h. The dashed lines indicate the position of prominent peaks in the Ppy control spectrum.*

those shown in Fig. 2 of the manuscript. This result shows that the formation of the Ppy is driven not by chlorophyll but rather by the photooxidative properties of the P_{700} reaction center of PSI.

SEM of Electrochemically Synthesized PPy

To compare the structure of the PSI-PPy composite, the morphology was investigated by SEM and compared to chemically synthesized and electrochemically synthesized PPy. Both the chemically (Fig. 3 in main manuscript) and electropolymerized (Fig. S2) polymers showed similar morphology with connected clumps of nanoparticles that is different from that of the composite.

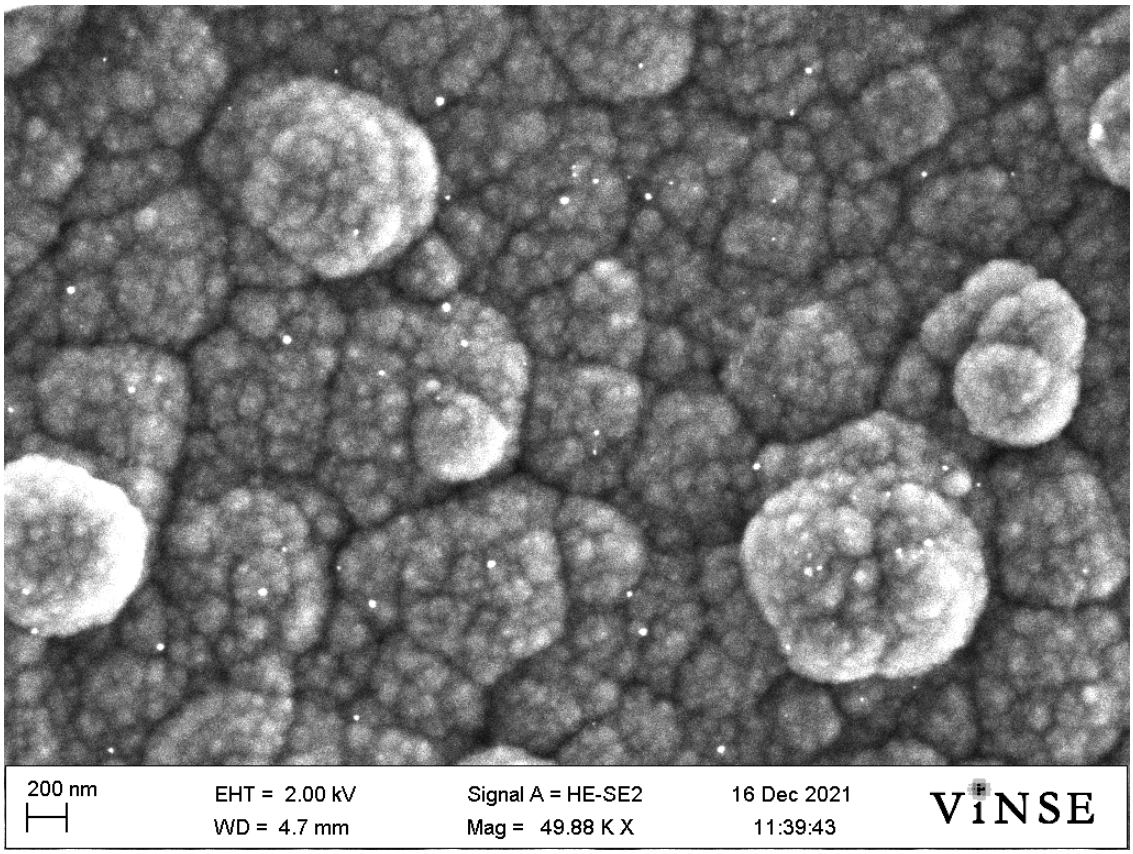

Figure S2 | *SEM of electropolymerized PPy grown on gold at a potential of 1 V for 30 s with $NaClO_4$ as a dopant.*

Confirmation of Successful Doping

To confirm that the $NaClO_4$ successfully doped the polypyrrole, EDS was performed to confirm the presence of Cl in the polymer. The imaged protein-polymer network had been rinsed with DI water, so no excess ions should appear unless they are connected to the network. The EDS spectra

in Fig. S3 show that there is a significant Cl signal coming from the polymer, confirming successful doping.

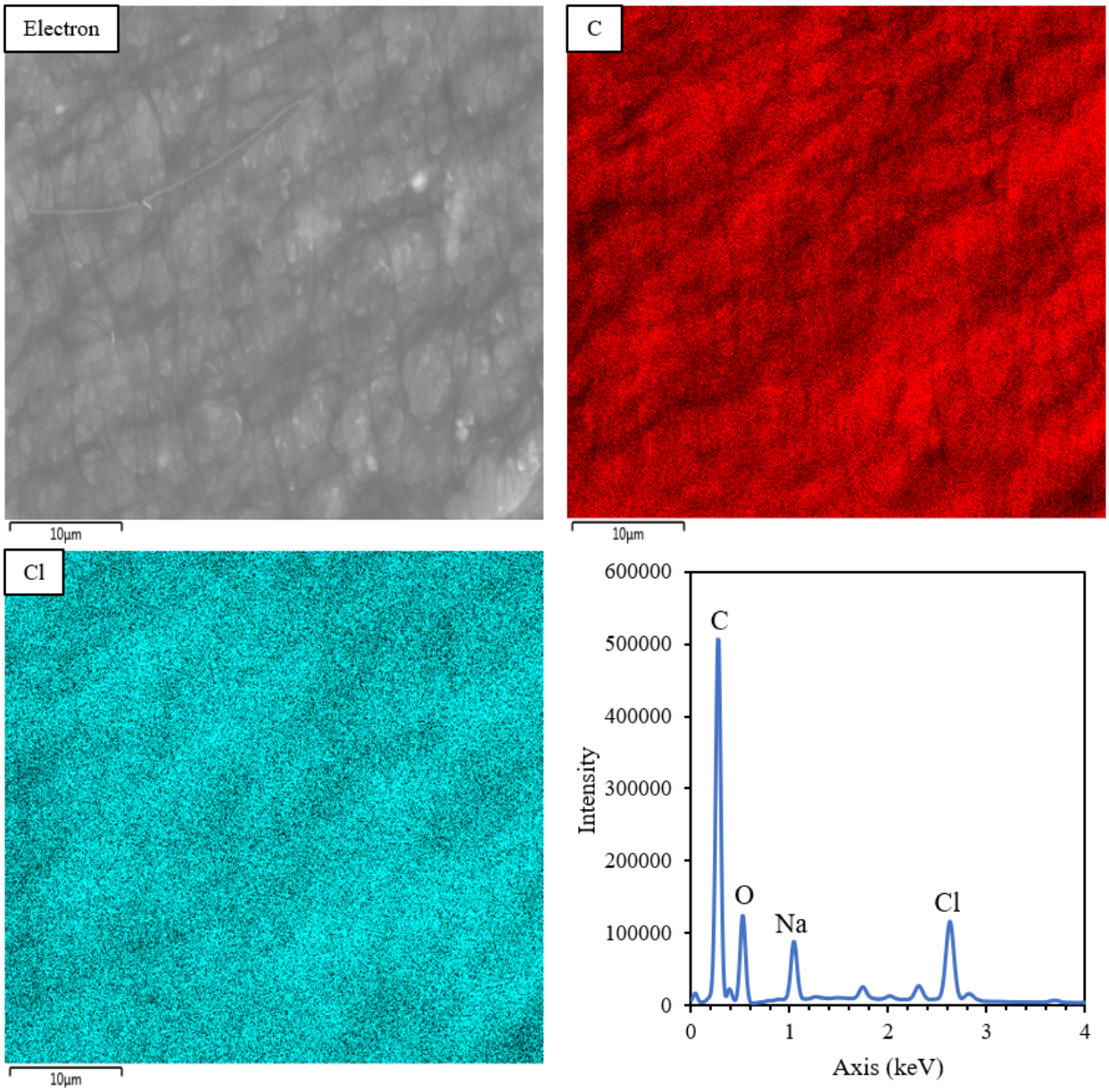

Figure S3 | *EDS map and spectra of PSI-PPy powder showing presence of Cl, indicating successful doping with* $NaClO_4$.

SDS-PAGE Analysis

The SDS-PAGE gel in Figure S4 shows a comparison of the PSI-Py reaction product to the monomer, PSI, UV-deactivated PSI with and without the monomer, and chemically polymerized

PPy with and without PSI. All of the samples were subjected to 6 h of illumination before being run through the gel.

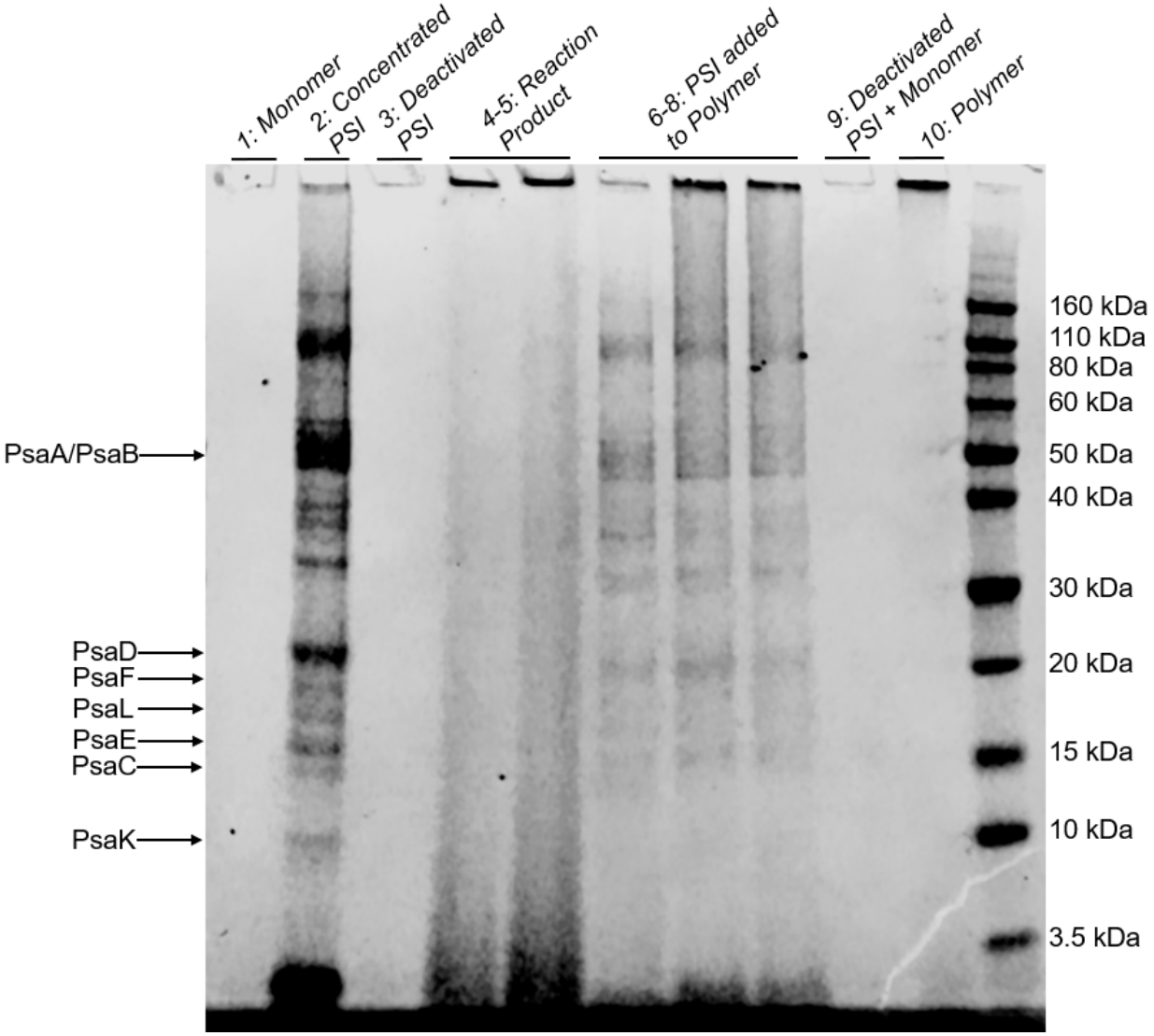

Figure S4 | *SDS-PAGE gel. Lane 1) 0.5 M monomer, lane 2) 20 μM unmodified PSI, lane 3) 20 μM UV-deactivated PSI, lanes 4 & 5) reaction product of 0.5 M monomer with 8 μM & 16 μM PSI, respectively, lanes 6, 7, 8) 4 μM PSI mixed with PPy chemically synthesized from 0.01 M, 0.1 M, and 0.5 M monomer concentrations, respectively, lane 9) 0.5 M monomer with 16 μM of UV-deactivated, lane 10) PPy chemically synthesized from 0.5 M Py, lane 11) reference ladder.*

The first 3 lanes are the monomer, free protein, and UV-deactivated free protein controls, respectively. No bands appear for the monomer or deactivated protein, but multiple bands appear in the unmodified free protein, with subunits PsaA and PsaB comprising the large band at 50 kDa.

Lanes 4 and 5 show the reaction product of PSI and Py monomer after 6 h of illumination. In these lanes, there is an appearance of a large mass collected at the top of the lanes and some streaking throughout the lower portion of the lanes. The band appears at the top of all the lanes

that are expected to have PPy in them (lanes 4, 5, 6, 7, 8, and 10). This band at the top is synthesized PPy that is unable to migrate through the gel because of either insolubility or extensive size. Lane 10 is the PPy control and the only present feature is the band collected at the top, confirming that the band is polymer.

In lanes 4 and 5 for the reaction product, the free protein bands seen in lane 2 are no longer present, which suggests strong interactions between the polymer and protein that could not be broken up by SDS. To ensure that the disappearance of the bands is not due simply to mixing of protein with polymer, PSI was added to differing concentrations of chemically synthesized PPy (lanes 6, 7, and 8). In these three bands, the free protein bands all appear alone with the polymer collecting at the top of the lanes. The presence of bands related to protein in lanes 6, 7, and 8 compared to the absence of bands in lanes 4 and 5 indicate that the protein interacts strongly with the polymer in a stable network. The absence of all free protein bands and not only the PsaA/PsaB subunits suggests that the protein is protected by the polymer from denaturation by the SDS.

PSI that is bleached by strong UV light shows no photoactivity and was used here as a control to address whether the polymerization reaction was due the photo-assisted redox capabilties of PSI or the presence of protein as a seeding site (lane 9). The absence of bands and polymer at the top of the well in the UV-deactivated protein samples, with and without monomer, show that there is no polymerization; thus, the polymer is formed by a photo-initiated reaction with PSI.

Analyzing the PSI-Ppy Composite with TGA and DSC

To compare the loss of PSI in both unmodified protein and in the protein-polymer composite, the TGA data were normalized to remove the behavior of the polymer based on the pure polymer curve (Fig. S5). The resulting normalization shows that PSI alone degrades at a faster rate than the PSI in the composite does, suggesting stabilizing interactions between the protein and polymer.

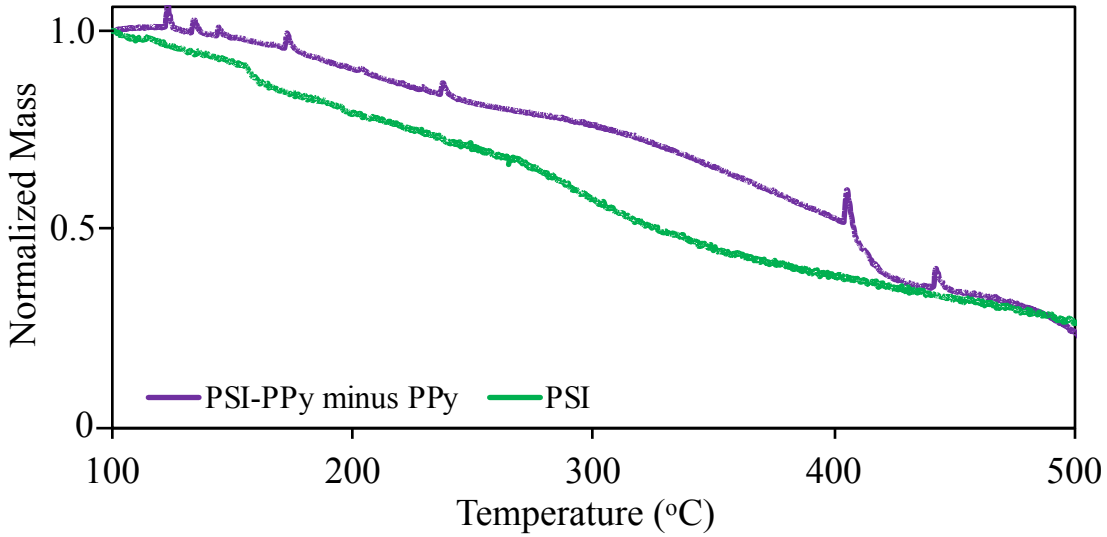

Figure S5 | *Normalized TGA comparing the relative mass loss of PSI in both the pure and PSI-PPy samples.*

Photoactivity of Bare Gold and PPy

PCA data was measured for both bare gold and electropolymerized PPy to show that any photoresponse is a result of PSI and not the substrate, polymer, or mediator system (Fig. S6).

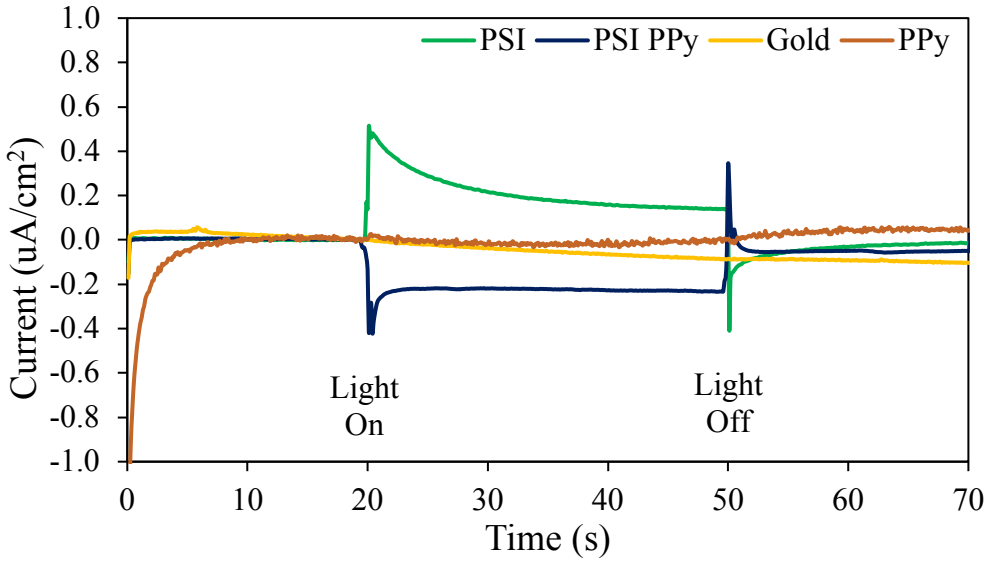

Figure S6 | *Photoresponse for PSI, PSI-PPy, PPy, and bare gold in 20:1 AscH:DCPIP mediator.*

Two-piston Conductivity Measurement Setup

The experimental setup used to measure conductivity and photoactivity for the PSI-PPy network powders is shown in Fig. S7. A transparent glass tube allows for light to reach the powder so that a photoresponse can be measured. The tube and the piston are made from a modified syringe tube with stainless steel plungers.

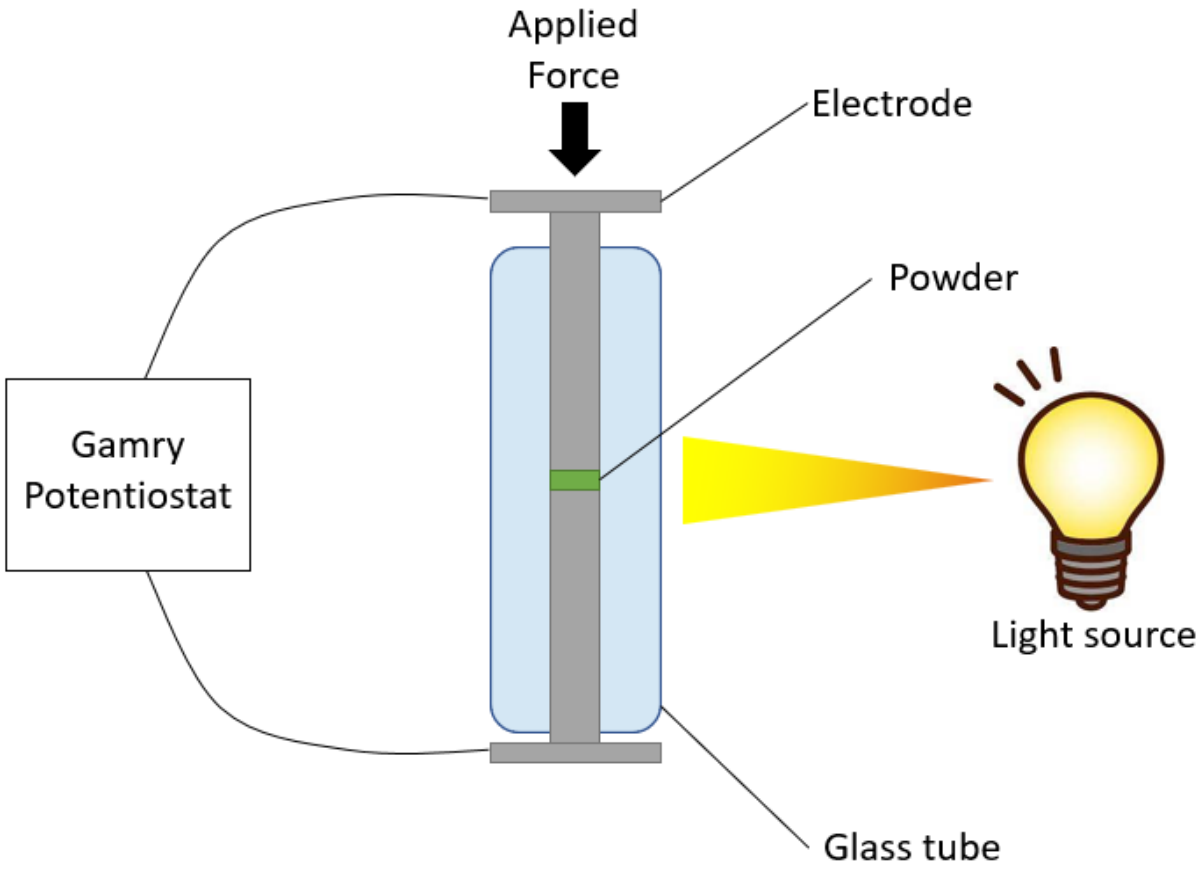

Figure S7 | *Two-piston experimental setup to measure conductivity and photoresponse for powder products.*