**Effect of Gold Underlayer on Copper (I) Oxide Photocathode Performance.**

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Supplementary information



**Figure S1**: XRD plot of a typical Cu2O film.

The Cu2O films electrodeposited on ITO on glass substrate. The electrodeposition was carried out at a current density of 0.5 mA/cm2 for 30 minutes. The XRD plot shows a dominant (111) crystallographic orientation.

The figures S2 and S3 show the photoelectrochemical performance of Au-Cu2O composite photocathodes in comparison to the control Cu2O photocathode. It has been observed that all the Au-Cu2O composite photocathodes demonstrate similar enhancements compared to the control Cu2O photocathode. The enhancement is close to 81%. The similarity in enhancement can be attributed to the difficulty in achieving monodispersed Au nanostrucutres.



**Figure S2:** The photocurrent density plots of Au-Cu2O composite photocathodes and control Cu2O photocathode. The Au nanostructures were fabricated at an applied potential of -0.8 V.



**Figure S3:** The photocurrent density plots of Au-Cu2O composite photocathodes and control Cu2O photocathode. The Au nanostructures were fabricated at an applied potential of -0.4 V.

The dark current was measured over a period of 1 h. For this measurement the working electrode was Au-Cu2O composite photocathode. A potential of -0.5 V vs Ag/AgCl, which was equivalent to 0 V vs RHE was applied for 1 h, in 0.5 M Na2SO4 electrolyte. Figure S4 shows the dark current for 1 h. The dark current approaches 0 mA/cm2 and remains constant through the entire experiment.



**Figure S4:** Dark current obtained from Au-Cu2O composite photocathode.

Admittance defines the ease with which carrier transport can occur. The ease of carrier transport was evaluated by measuring the diameter of the semicircle, which is a characteristic of each admittance plot. The larger the diameter, easier is the carrier transport. Admittance is a reciprocal of impedance (Y´ = 1/Z´) and is measured in siemens. Figure 12 presents admittance plots of Au, Cu2O and Au-Cu2O samples. From the admittance plot, it was clear that Au sample demonstrated an ease of carrier transport from the electrode to the electrolyte or greater conductance. However, the Cu2O exhibited less ease in carrier transport or less conductance. The admittance plot of Au-Cu2O sample exhibited a greater ease in carrier transport than Cu2O sample or higher conductance than Cu2O.



**Figure S5:** Admittance plots of Au, Cu2O and Au-Cu2O samples.



**Figure S6:** Absolute quantum efficiency for Cu2O and Au-Cu2O samples.