Supplemental Informations:

1.1 Synthesis of CuO films

The CuO films were fabricated on ITO substrates by electrodeposition method. Firstly, an alkaline aqueous solution composed of 0.48 M $CuSO_4 \cdot 5H_2O$ aqueous solution stabilized 3 M $C_3H_6O_3$. Then, the pH value of mixture solution wad adjusted to 10 and the solution was maintained at 35 °C. The Cu_2O films were electrodeposited a potential of -0.5 V vs. Ag/AgCl for 20 min. After drying at room temperature, the as-prepared Cu_2O films were annealed in air at 500 °C for 1 h to obtain CuO films.

1.2 Synthesis of CuO/Al and CuO/Al/Al_2O_3 films

The Al nanoparticles were deposited onto the surface of CuO films through magnetron sputtering method. The deposition was carried out at room temperature using Al target and the thickness of Al layer was controlled to be 20 nm. After deposition, the pure CuO/Al films had been obtained. Finally, the prepared CuO/Al films subjected oxidation in air that leads to the external conversion of the Al NPs into ultrathin Al_2O_3 passivation layer, thereby forming CuO/Al/Al_2O_3 films.

1.3 Characterizations

The morphology of the as-prepared films were investigated by scanning electron microscope (SEM, HITACHI S-4800I) and transmission electron microscopy (TEM, JEOL JEM-2100). The energy dispersive X-ray spectroscopy (EDS, AZtec from Oxford) was used to characterize the elements of samples. The crystalline structures of samples were performed by X-ray diffraction (XRD, Rigaku-D/max-2500, Cu Kα radiation, 40 kV, 150 mA). X-ray photoelectron spectroscopy (XPS) analyses were performed on a Thermo ESCALAB 250XI system with an Al-Kα X-ray source (hν=1486.6 eV). The optical properties of the samples were measured by UV-vis diffuse reflectance using an ultraviolet-visible spectrophotometer (UV-Vis, DU-8B). The surface photovoltage (SPV) measurements were carried out on a surface photovoltage spectrometer (PL-SPS/IPCE1000). The PEC performances of the samples were examined in a three-electrode cell using a Pt plate and an Ag/AgCl electrode as the counter electrode and reference electrode, respectively. The electrolyte was 1 M KOH (pH=13.6) aqueous solution.

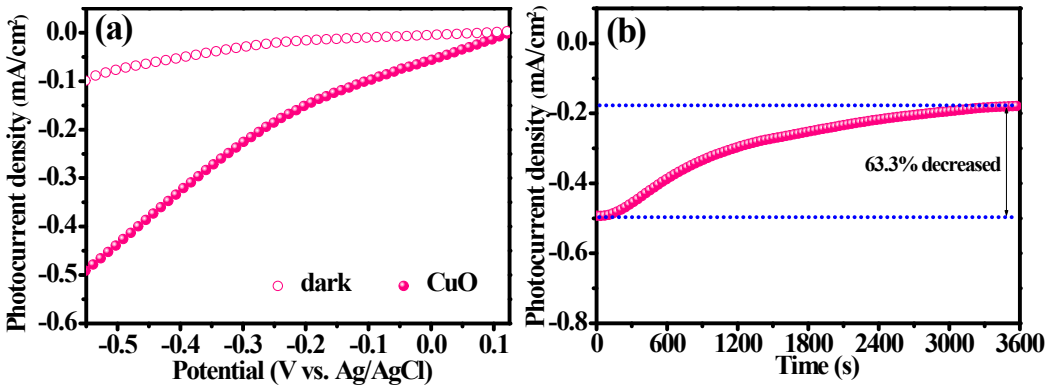

Fig.S1 Photocurrent density-voltage (J-V) curves (a) and photocurrent density-time curves measured in 1 M NaOH electrolyte at -0.55 V vs. Ag/AgCl under simulated sunlight illumination for 1 h of CuO

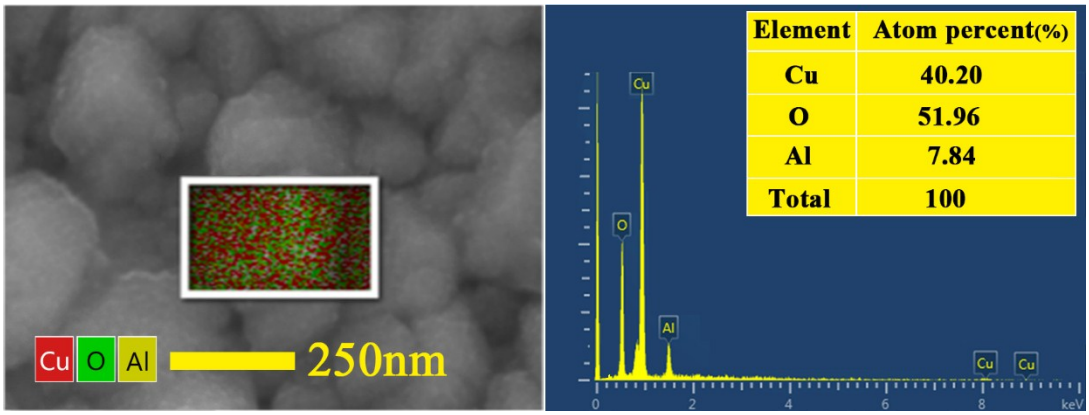

Fig.S2 The corresponding EDS spectrum of CuO/Al/Al_2O_3

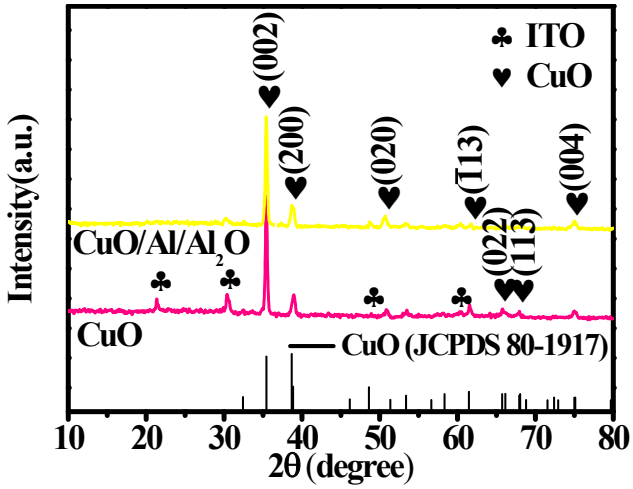

Fig.S3 XRD patterns of CuO and CuO/Al/Al_2O_3

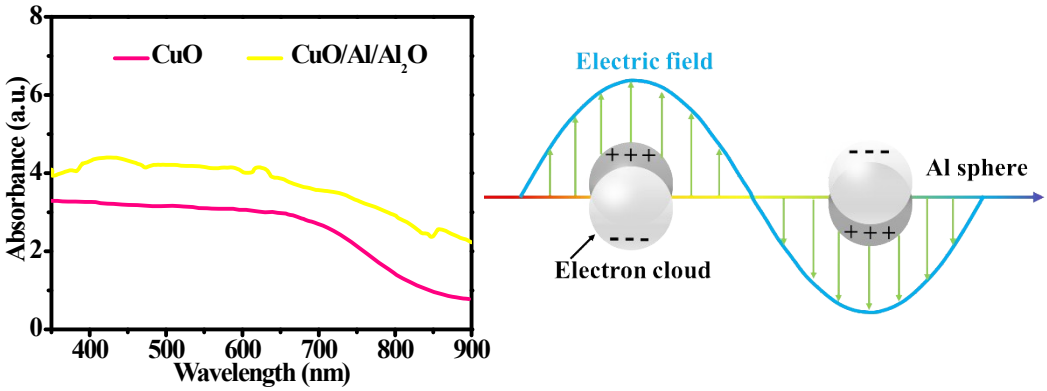

Fig.S4 UV-vis spectra of CuO and CuO/Al/Al_2O_3; the right side part is the schematic diagram of localized surface plasmon for a spherical Al nanoparticle

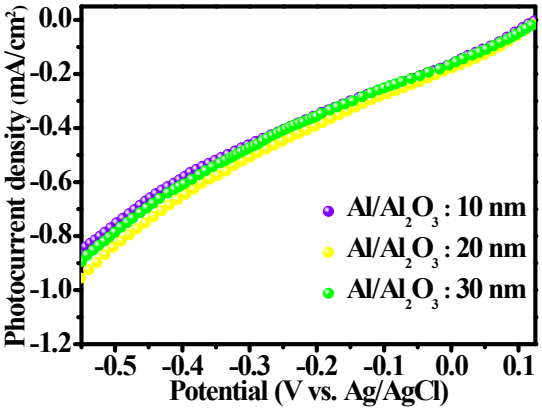

Fig.S5 Photocurrent density-voltage curves of CuO/Al/Al_2O_3 with different Al layer thickness

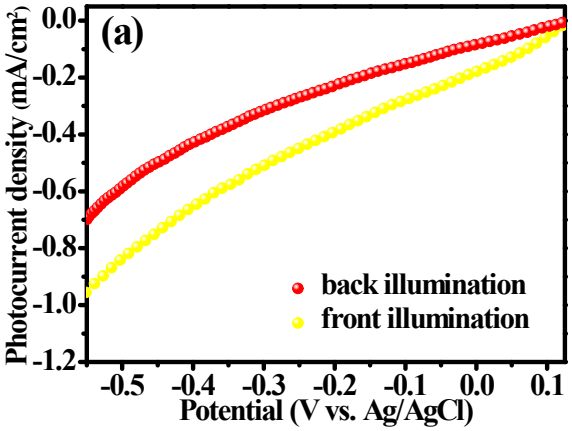

Fig.S6 Photocurrent density-voltage curves of CuO/Al/Al_2O_3 under back and front illumination

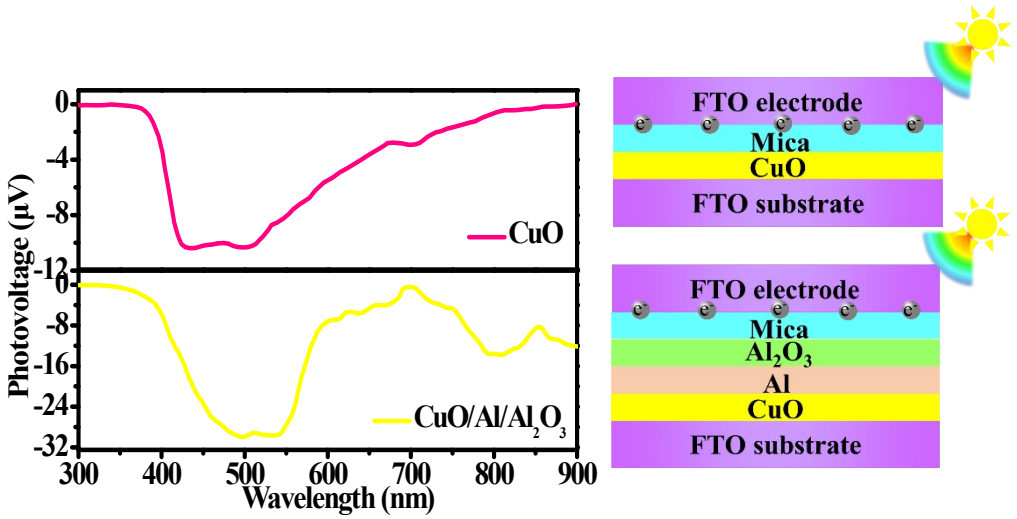

Fig.S7 Surface photovoltage spectroscopy of CuO and CuO/Al/Al_2O_3 composite with front illumination; the right side part is the corresponding schematic diagram of SPV measurement configuration

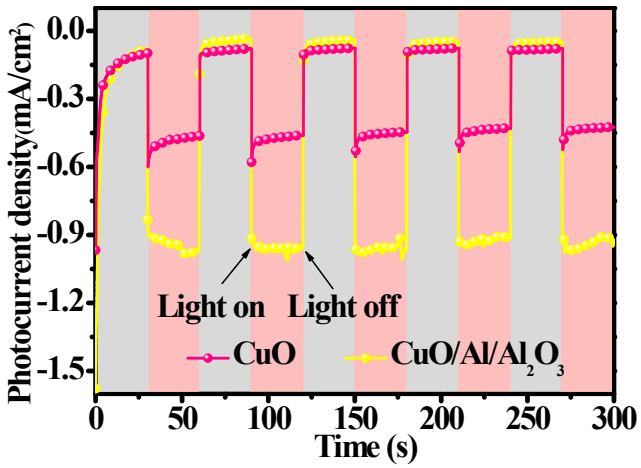

Fig.S8 Photocurrent density-time (J-t) curves with 30 s light on/off cycles of CuO and CuO/Al/Al_2O_3

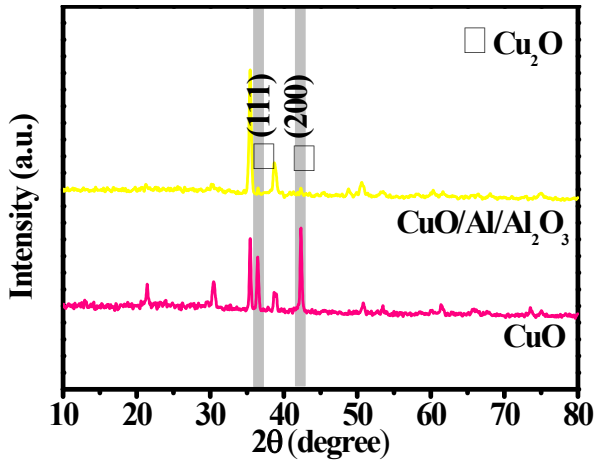

Fig.S9 XRD patterns of CuO and CuO/Al/Al_2O_3 after 1 h PEC stability test

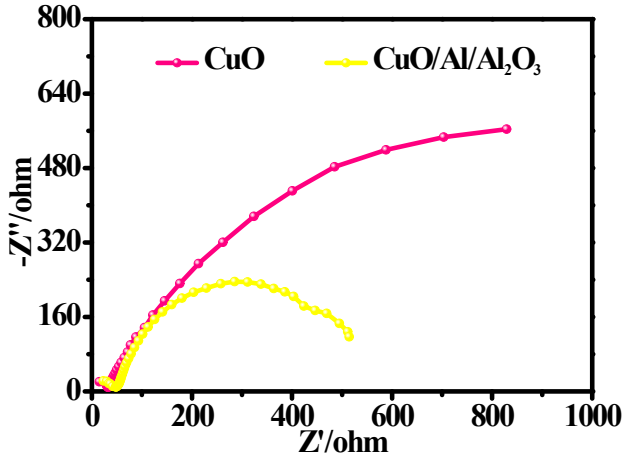

Fig.S10 Nyquist plots measured at -0.55 V vs. Ag/AgCl of CuO and CuO/Al/Al_2O_3