Electronic structure, photovoltage, and photocatalytic hydrogen evolution with p-$CuBi_2O_4$ nanocrystals

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Supporting Information
(4 pages)

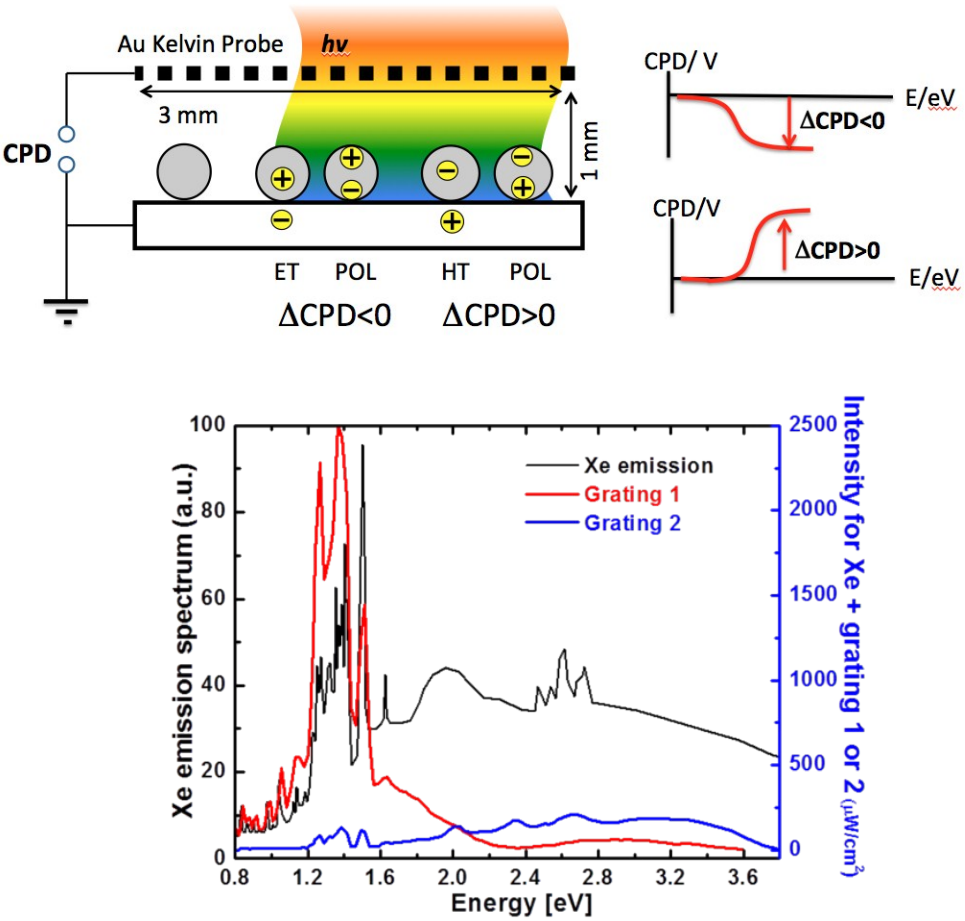

Figure S1. SPS measurement configuration and emission spectrum of light source (Grating 2 was used for all measurements)

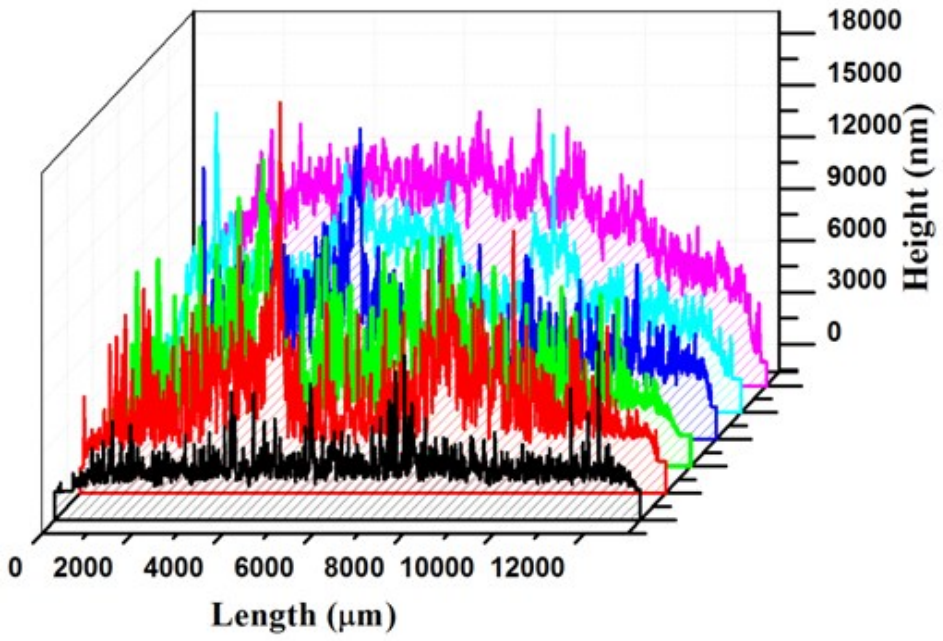

Figure S2. Profilometry scans of $CuBi_2O_4$ films on FTO with different thickness.

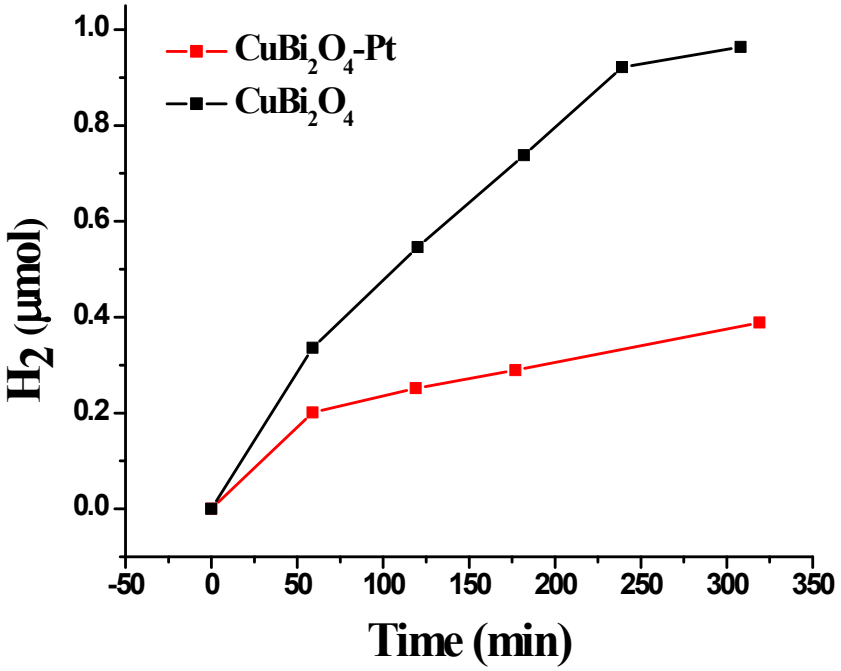

Figure S3. H_2 evolution from 50 mg $CuBi_2O_4$ nanoparticles in 100 mL of aqueous methanol (20% v/v) solution under visible light (> 400 nm, 240 mW cm^{-2} at flask), before and after addition of a Pt cocatalyst. The lower activity of the platinated material is attributed to photocorrosion of $CuBi_2O_4$ during photodeposition of Pt. Conditions: 50 mg of $CuBi_2O_4$ was dispersed in a solution of H_2PtCl_6 (1 mol % Pt) and 10% methanol in water and irradiated two hours with unfiltered light from a 300 W Xe arc lamp. Platinated powders were washed repeatedly with pure water before use.

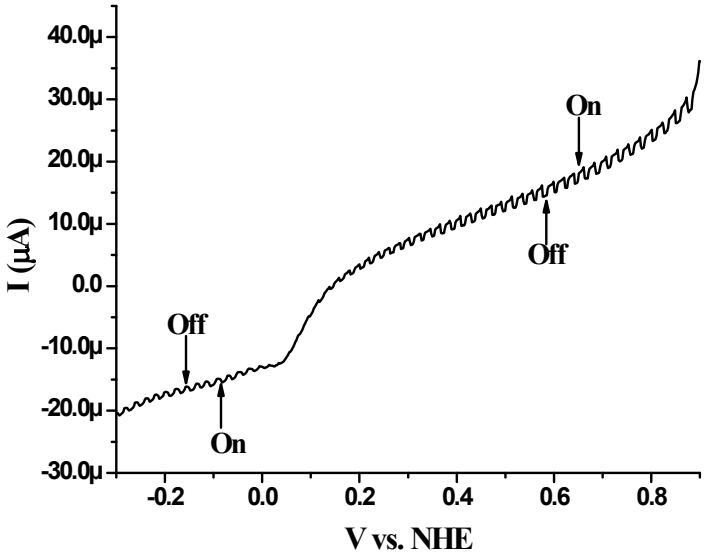

Figure S4. Photoelectrochemical scan on $CuBi_2O_4$ nanocrystal film on FTO substrate in 0.1 M K_2SO_4 under Xe – illumination (full spectrum, 40 mW cm^{-2}).

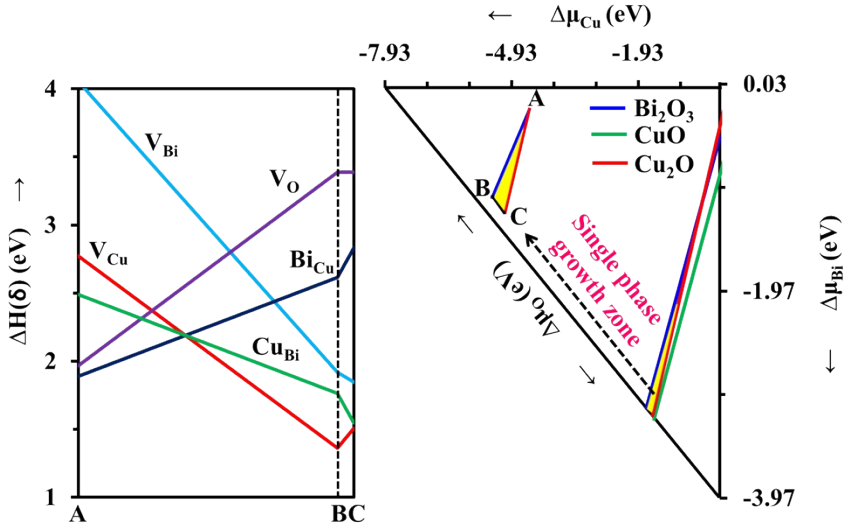

Figure S5: The left figure represents the probability of forming different intrinsic defects in $CuBi_2O_4$ with respect to its single-phase growth region (see yellow bounded region at right figure); the yellow region in the left figure was achieved using the chemical potenial landscapre analysis (for detail

methodology, see ref. 1[1]). ΔH is the defect formation energy. In the right figure, $\Delta\mu_\alpha$ (α = Cu, Bi, and O) axes correspond to growth conditions, from rich ($\Delta\mu_\alpha$ = 0 eV) to poor ($\Delta\mu_\alpha$ = formation enthalpy), of respective species. The values of A, B, and C in the figure are ($\Delta\mu_{cu}$ = -0.33 eV, $\Delta\mu_{Bi}$ = -0.96 eV, $\Delta\mu_O$ = -1.42 eV), ($\Delta\mu_{cu}$ = -1.74 eV, $\Delta\mu_{Bi}$ = -3.10 eV, $\Delta\mu_O$ = 0 eV), and ($\Delta\mu_{cu}$ = -1.60 eV, $\Delta\mu_{Bi}$ = -3.17 eV, $\Delta\mu_O$ = 0 eV), respectively.

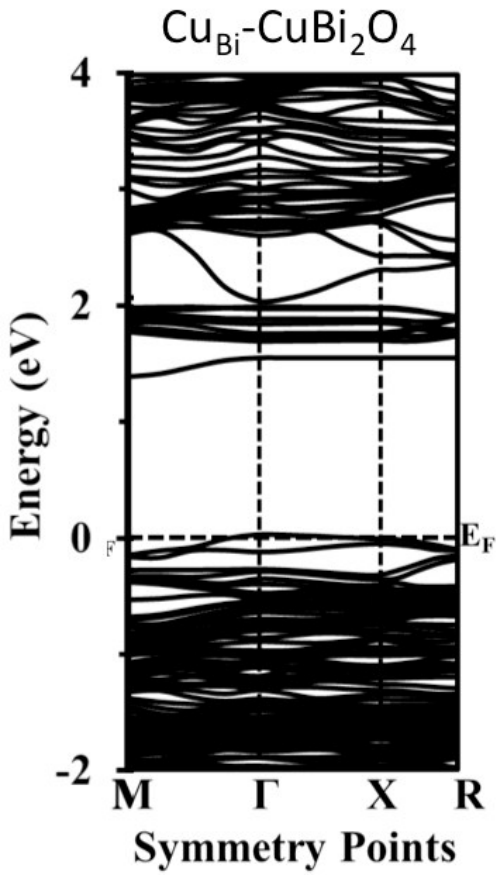

Figure S6. The DFT+U electronic band structure of Cu_{Bi} - $CuBi_2O_4$.

Reference:

1 P. Sarker, M. M. Al-Jassim and M. N. Huda, *J. Appl. Phys.*, 2015, **117**, 035702.