Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Low temperature grown $CuBi_2O_4$ flower morphology and its composite with CuO nanosheets for photoelectrochemical water splitting

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Supplementary Information

ESI-I

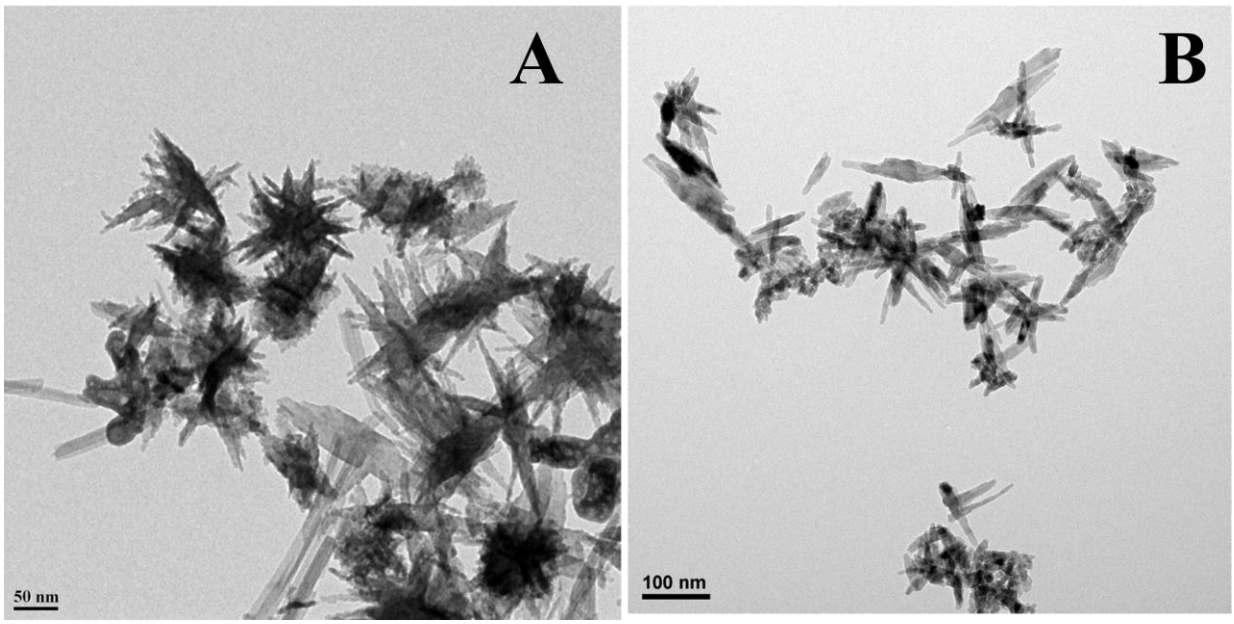

Figure ESI-I: TEM images of nonstoichiometric Cu : Bi 5:1 (A) and 15:1 (B) cases.

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ESI-II

The TEM images of $CuBi_2O_4$ (A) show nanorod assembled spherulitic structures and of pure CuO (B) show thin sheets-like morphology.

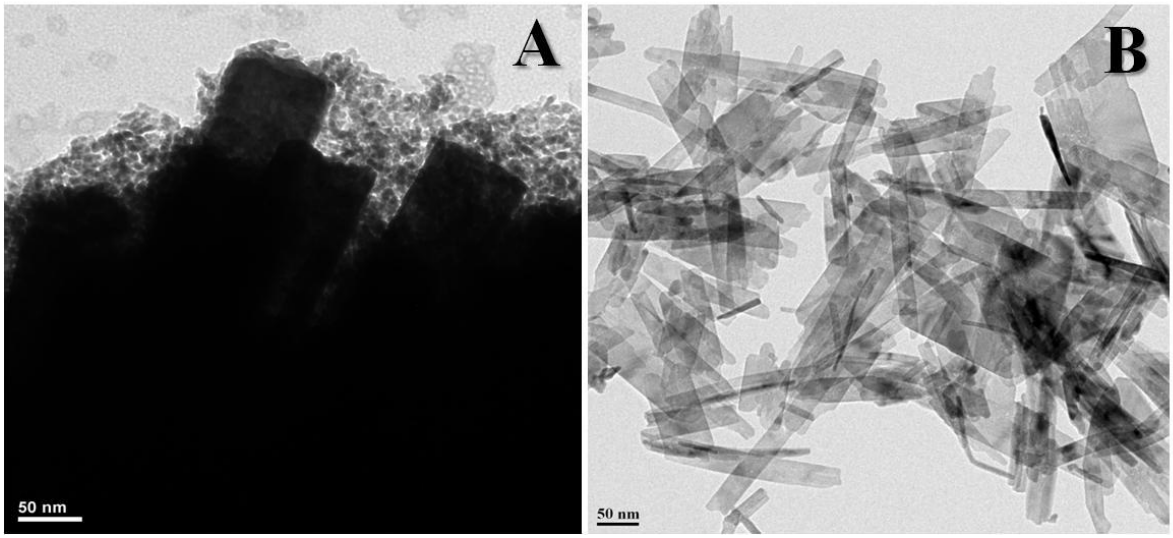

Figure ESI-II: Individual TEM images of pure $CuBi_2O_4$ (A) and pure CuO (B).

ESI-III

The comparative PEC performance of pure $CuBi_2O_4$, CuO and $CuBi_2O_4$-CuO composite with different non stoichiometric cases.

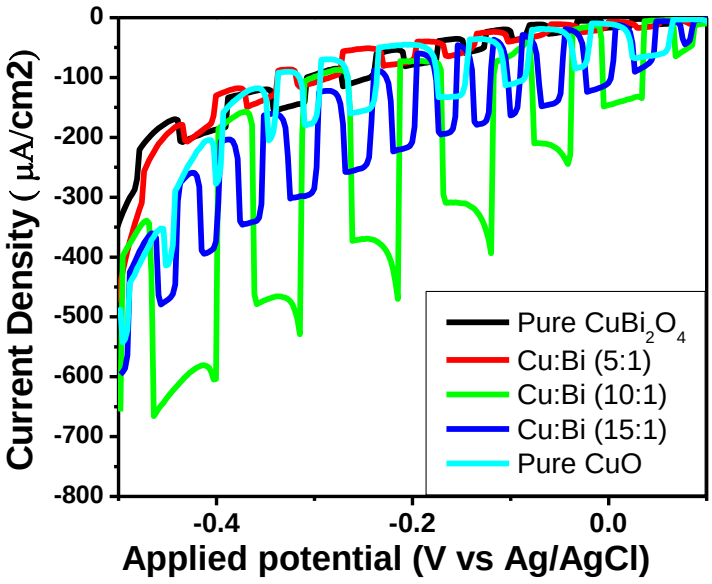

Figure ESI-III: Photoelectrochemical performance of pure $CuBi_2O_4$, CuO and all nonstoichiometric cases

ESI-IV

In order to determine the conduction/valance band positions and relative band alignment of $CuBi_2O_4$ and CuO, we performed cyclic voltammetry. For this we used thin films of $CuBi_2O_4$ and CuO coated onto FTO-glass as working electrodes in a typical three electrode set up. The electrolyte used was 0.1 M Na_2S, which is same as the one for photoelectrochemical measurements. Ferrocenemethanol was used as a standard. At first a cyclic voltammogram of ferrocenemethanol, dissolved in 0.1M Na_2S, was recorded (under the same three electrode set up) and the oxidation/reduction peaks were identified. From the redox peaks the $E_{1/2}$ potential of ferrocenemethanol was determined. Then from the cyclic voltammogram of $CuBi_2O_4$ and CuO, separately, the corresponding onsets of oxidation peaks were recorded[1,2]. The absolute position of the highest occupied molecular level (E_{HOMO}) Or Valance band was determined using the equations presented below (for the case of $CuBi_2O_4$). From the optical band gap obtained using Tauc plot measurement, the absolute position of the conduction band was determined. The relative band alignment obtained from this method was presented in Figure ESI-IV b.

$E_{1/2}$ (Ferrocenemethanol) = ($E_{Reduction}$ + $E_{Oxidation}$) /2 = 0.18 V

$E_{Oxd} = E_{oxd}$ ($CuBi_2O_4$) - $E_{1/2}$ (Ferrocenemethanol)

E_{VB} ($CuBi_2O_4$) = - (E_{oxd} + 4.8)

Hence For $CuBi_2O_4$: E_{VB} = -5.46 w.r.t Vacuum or +0.96 w.r.t NHE

Bandgap of $CuBi_2O_4$ as per optical data is 1.74. Hence E_{CB} = -3.72 w.r.t Vacuum or -0.78 w.r.t.NHE

For CuO: E_{VB} = -5.1 w.r.t Vacuum or +0.7 w.r.t NHE

Bandgap of CuO as per optical data is 1.35. Hence E_{CB} = -3.75 w.r.t Vacuum or -0.85 w.r.t. NHE

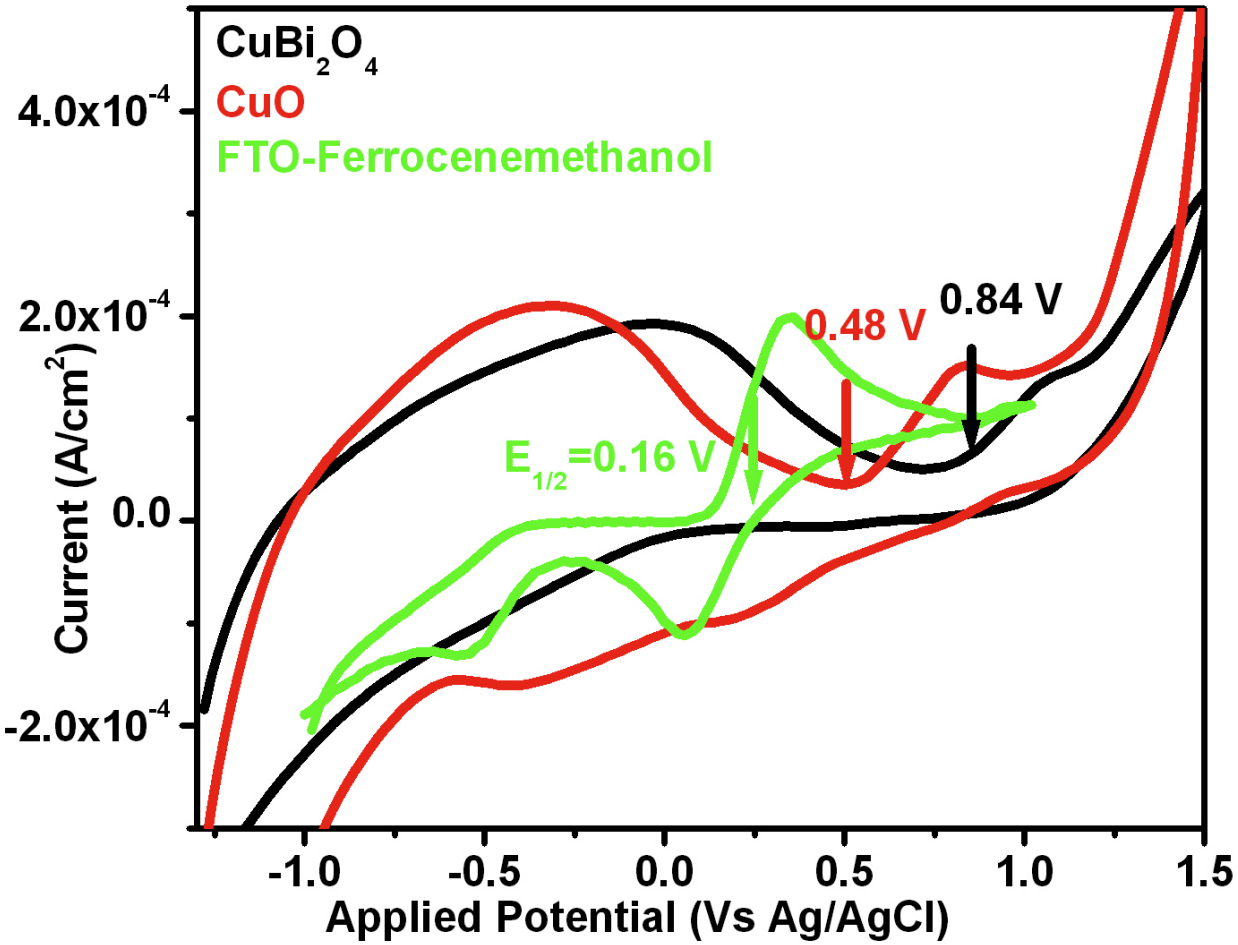

Figure ESI-IV a: Cyclic voltammograms of $CuBi_2O_4$ and CuO

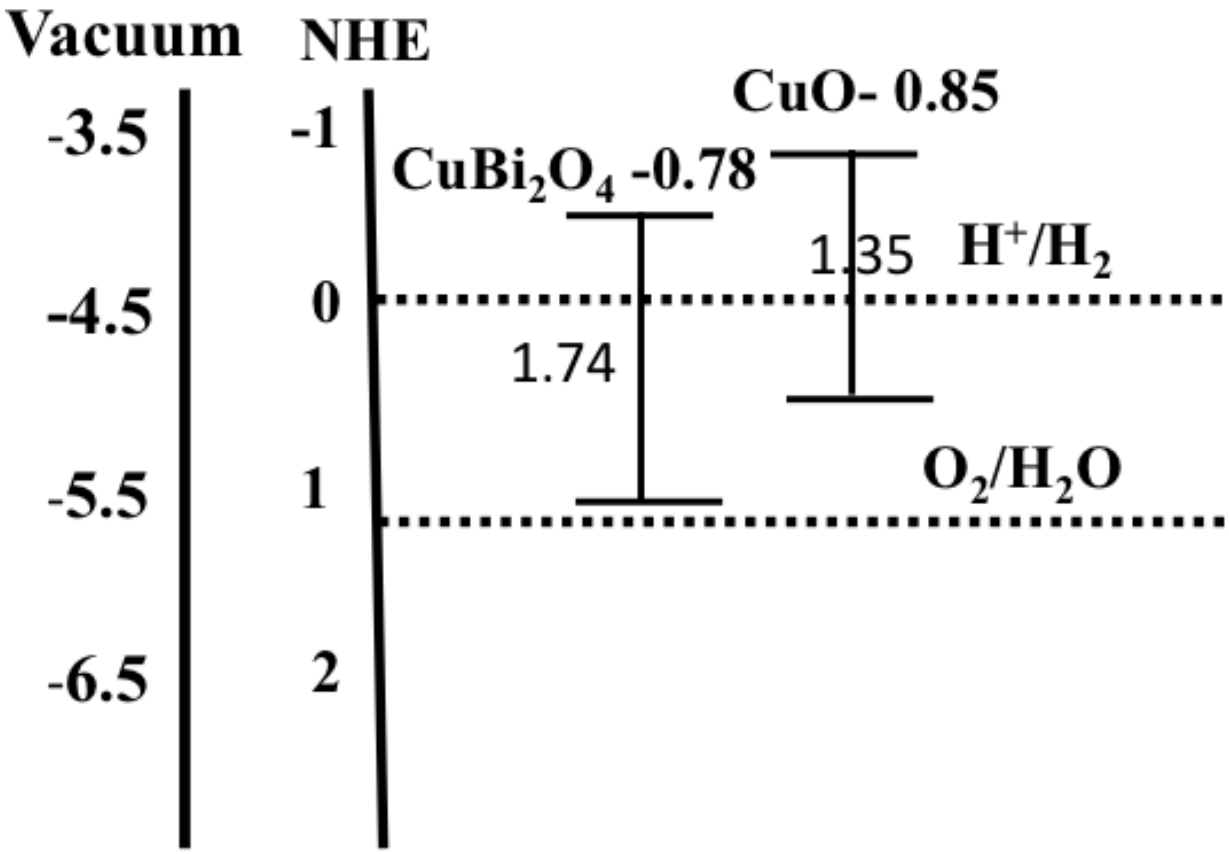

Figure ESI-IV b: Relative band alignment of $CuBi_2O_4$ and CuO obtained from cyclic voltammetry.

1. L. Ding, D. Jiang, J. Huang, G. Erdan, L. Liu, Z. Chai, and D. Liu, J. Phys. Chem. C, 2008, **112**, 10266-10272.
2. W. You, L. Wang, Q. Wang, and L. Yu, Macromolecules, 2002, **35**, 4636-4645

ESI-V

All the photoelectrodes were prepared by doctor blading the paste of the respective photocatalyst onto FTO-coated glass and consequently annealing at 400 ^{0}C for an hour. In order to make sure if this heat treatment caused any changes in the morphology or structures of the respective catalysts, we performed FESEM of the heat-treated coatings. As can be seen below, there is not any remarkable change in the morphology of any of the photocatalyst. However some extent of necking is definitely observed due to sintering effects.

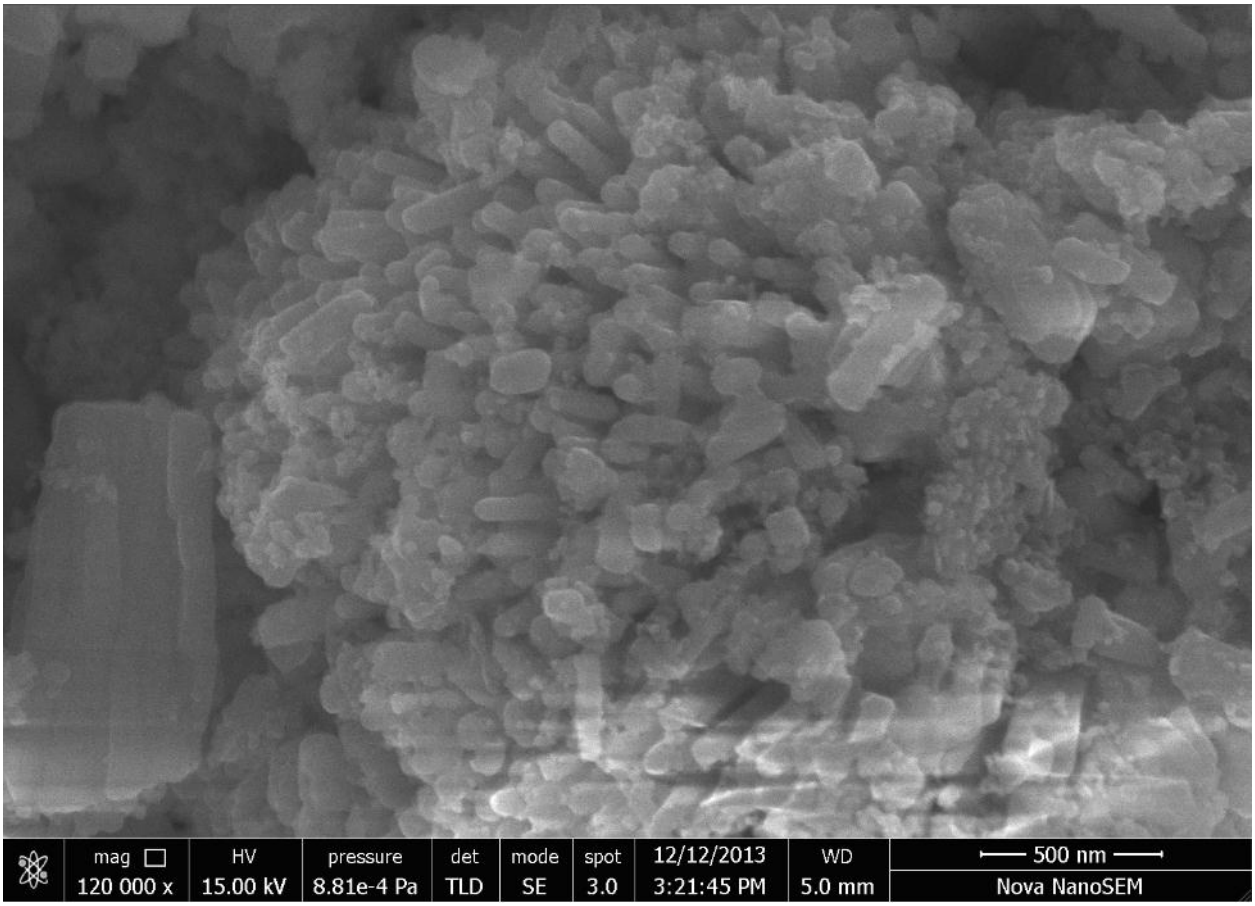

Figure ESI-V a: FESEM image of heat-treated pure $CuBi_2O_4$ photocathode

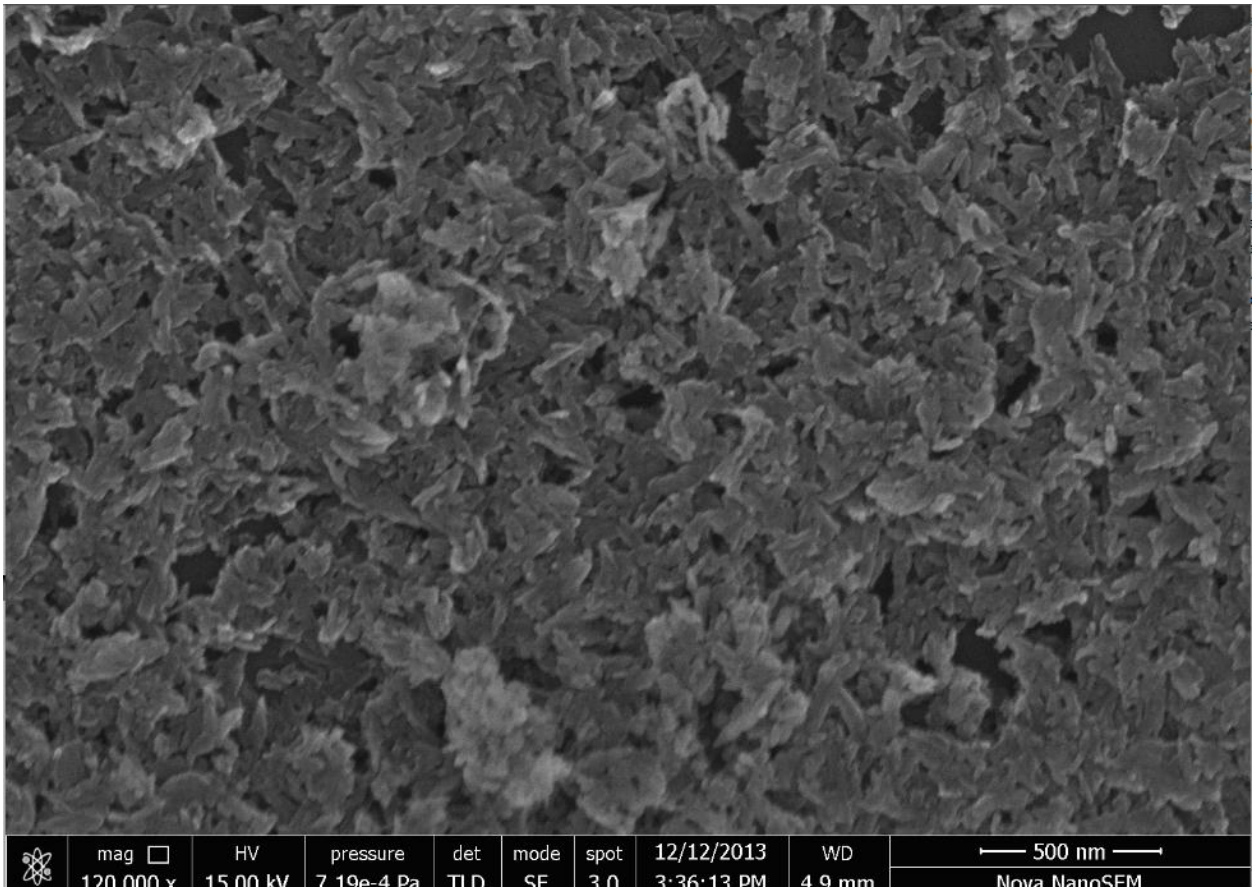

Figure ESI-V b: FESEM image of heat-treated pure CuO photocathode

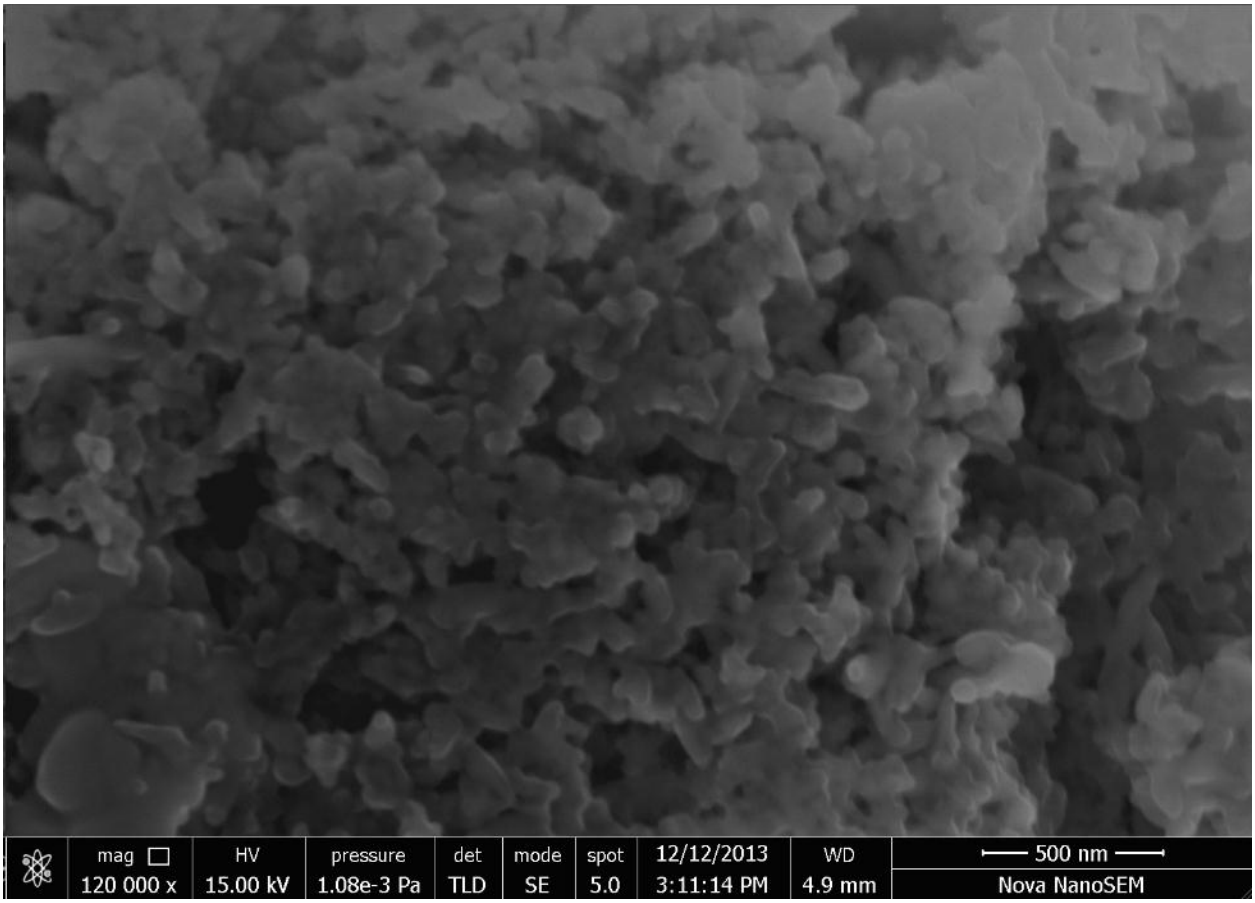

Figure ESI-V c: FESEM image of heat-treated nanocomposite $CuBi_2O_4$-CuO photocathode