

Supplementary Information

Synthesis and Evaluation of CoPc Grafted Bismuth Oxyhalide ($\text{Bi}_{24}\text{O}_{31}\text{Br}_{10}$): A Visible Light-Active Photocatalyst for CO_2 Reduction into Methanol

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1.1. HR-TEM images and elemental composition

The HR-TEM images of the semiconductor showed hexagonal and spherical shape of the particles at 20 nm (Figure S1). The inter-planer distance (d) values at 0.284 and 0.309 nm corresponding to (117) and (213), respectively.¹ SAED confirmed the crystallinity of the semiconductor due to the presence of bright spots (Figure S1e). The elemental composition of bismuth, bromine, and oxygen represented in the EDX pattern of BOB confirmed the presence of Bi, Br, and O (Figure S1f). The elemental mapping indicated the significantly higher concentration of Bi as compared to the O in the semiconductor BOB (Figure S2).

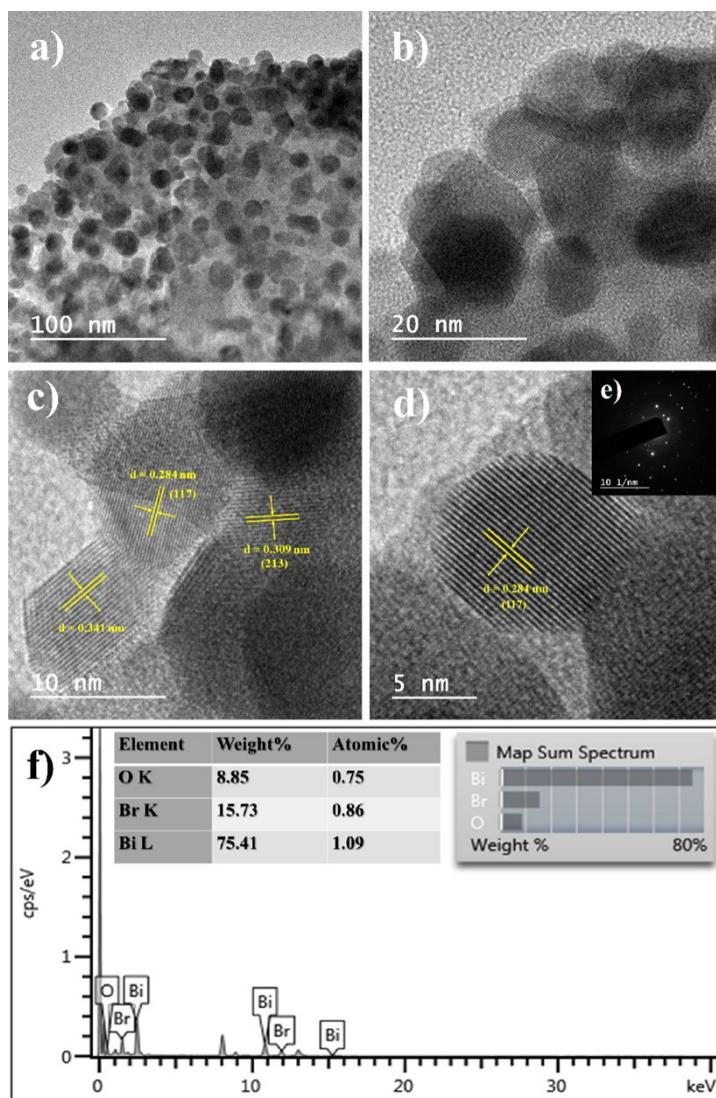


Figure S1. HR-TEM images and EDX pattern of BOB semiconductor **1**

1.2. Elemental mapping of $\text{B}_{24}\text{O}_{31}\text{Br}_{10}$ semiconductor

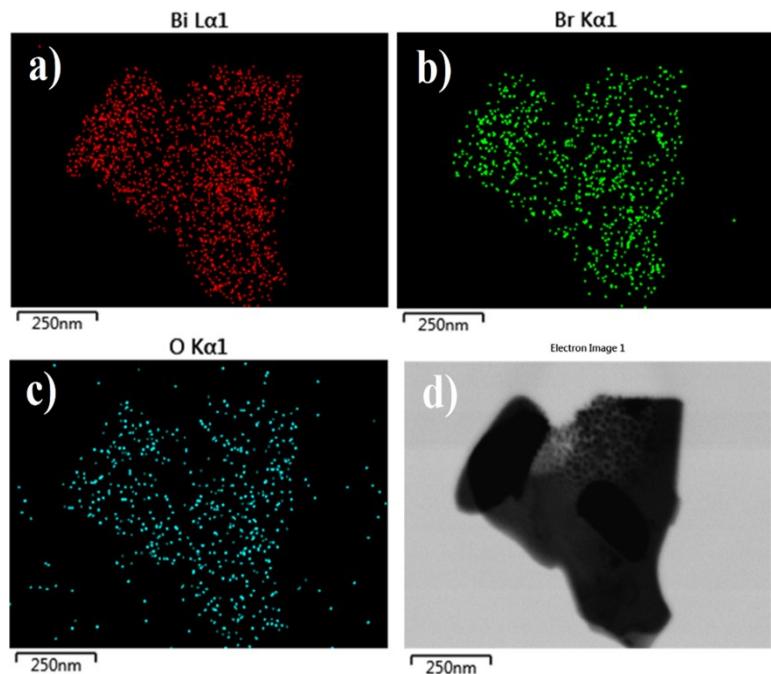


Figure S2. Elemental mapping of a) Bi, b) Br, c) O and d) electron image in BOB semiconductor.

1.3. Thermal degradation pattern

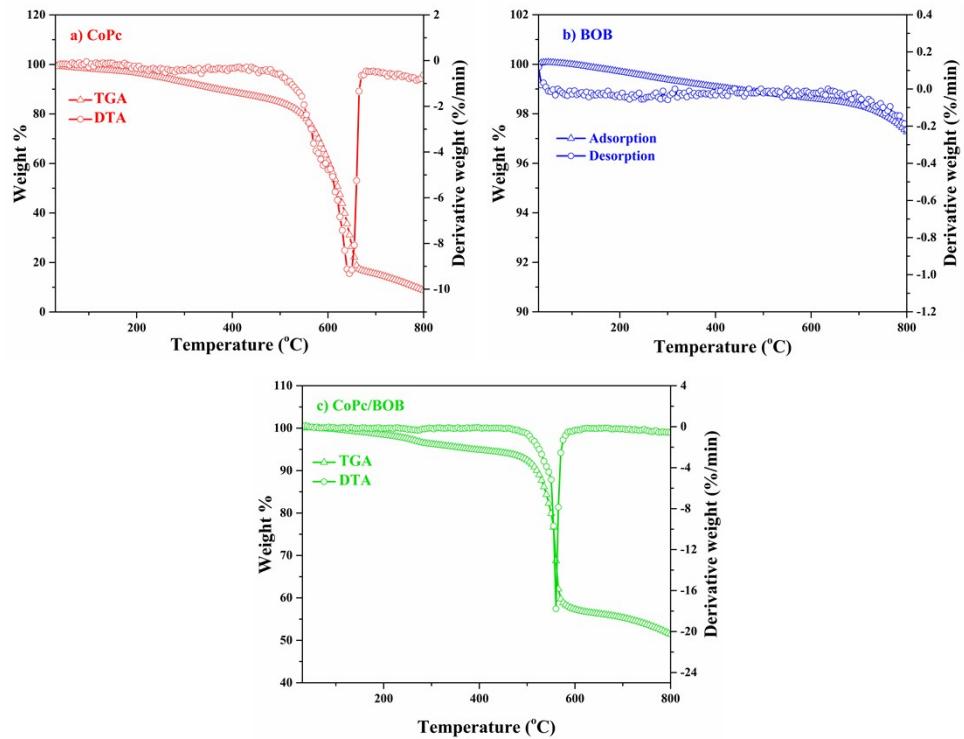


Figure S3. TG-DTA of a) CoPc, b) BOB and c) CoPc/BOB hybrid

1.4. Re-purging experiment for evaluation of photocatalyst stability

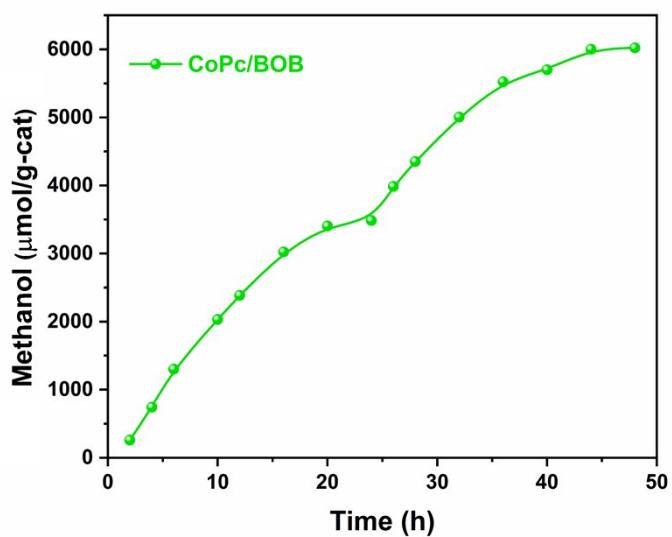


Figure S4. Repurging experiment

1.5. Calibration curve for methanol

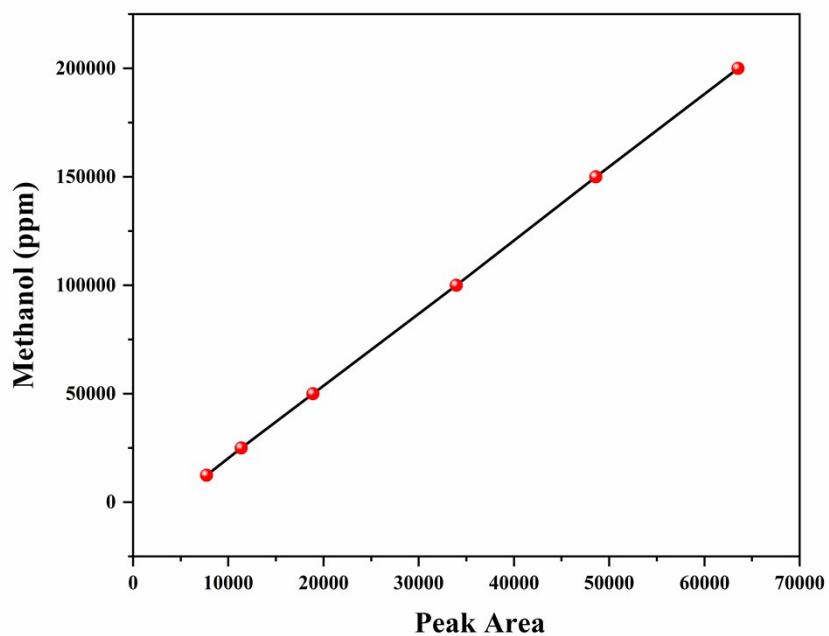


Figure S5. Calibration curve for methanol quantified by GC-FID

1.6. GC-FID chromatogram

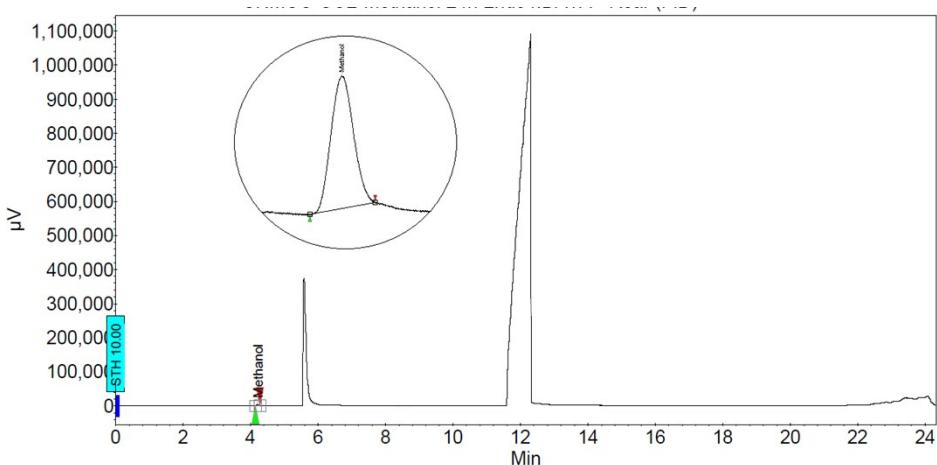


Figure S6. GC-FID chromatogram of the reaction mixture after 24 h of irradiation using CoPc/BOB photocatalyst

References

1. Z. Liu, J. Niu, P. Feng, Y. Sui and Y. Zhu, *RSC Adv.*, 2014, **4**, 43399-43405.